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REFRACTIVE INDEX AND DISPERSION OF DISTILLED WATER FOR VISIBLE RADIATION, AT TEMPERATURES 0 TO 60° C

By Leroy W. Tilton and John K. Taylor

ABSTRACT

All known requisites for precision and accuracy within $\pm 1 \times 10^{-6}$ in refractive index were employed in these determinations made by the minimum-deviation method using specially designed hollow prisms and platinum resistance thermometers. The data were adjusted by least squares and are represented by a general formula having 13 constants, the average of the 133 residuals being 1.2×10^{-6}. A general double-entry table of refractive indices (6,776 listings) with temperature and wave length as arguments has been computed to yield sixth-decimal data by linear interpolation. The maximum refractivity of water is found to be near 0° C, but the exact temperature thereof is a function of wave length, with a total variation of approximately 0.5° C for the visible spectral range. Other more specific tables of indices are given, and evidences of slight systematic errors are discussed. The attained precision is approximately as expected, but there is marked disagreement with some of Flatow's indices, which have been widely used and are the basis for the data on water as given in the International Critical Tables. The authors' opinions concerning the accuracy of their results are qualitatively confirmed by the medial relation of their data to all of those previously published, and quantitatively, within the temperature range 0 to 16° C, there is remarkably close agreement with the interferometrically determined indices of water, as reported by Mlle. O. Jasse.

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I. INTRODUCTION

Precise and accurate measurements on the properties of distilled water are desirable because this substance provides such a very suitable and convenient standard easily obtainable in a highly purified state. This has long been recognized in the calibration and standardization of volumetric apparatus, and very elaborate measurements of the density of water, to six and seven decimals, are available through the work of M. Thiesen [1] and of P. Chappuis.[2] Moreover, investigations of recent years on the isotopic composition of water have shown that this confidence in its uniformity is justified, the density of ordinary surface waters being constant, after purification, to better than 1 part in 1,000,000.[3]

1. PURPOSE OF THESE DETERMINATIONS

For refractive-index measurements many refractometers permit rapid and precise readings to the fifth decimal place and are used over a wide range in temperatures, for both scientific and industrial purposes. In testing, calibrating, and using these refractometers the correctness of their readings for some comparison standard is a matter of primary importance and, of liquids, distilled water is the standard medium most widely used for this purpose. Consequently, an accurate knowledge of the refractivity of water for the sodium lines, and of its variation with temperature, is required. An extension of such knowledge to other wave lengths is desirable, not only because technical applications of refractometry are being extended throughout the visible spectrum, but also in order to supply accurate initial data that will permit using an interferometer and the "method of coincidences" for the confirmation or revision of existing data.[4]

2. VARIATIONS IN PUBLISHED VALUES OF THE INDEX OF WATER

Published data on the refractivity of water are so completely presented by Dr. N. E. Dorsey [5] of this Bureau, that a complete bibliography appears unnecessary here. Several graphs, however, are presented to show at a glance the results obtained by previous investigators. These data are plotted in figures 1 to 6, and for convenience of comparison the plotting is with respect to the NBS values reported in this paper. In some cases this has involved an extrapolation of

[1] Wiss. Abhandl. physik. tech. Reichsanstalt **4**, 1 to 32 (1904).
[2] Travaux et Mémoires du Bureau International des Poids et Mesures **13**, D39 (1907). See also J. Research NBS **18**, 213 (1937) RP971.
[3] See, for example, E. R. Smith and H. Matheson, J. Research NBS **17**, 627 (1936) RP932; E. W. Washburn and E. R. Smith, BS J. Research **12**, 305 (1934) RP656; A. F. Scott, Science **79**, 565 (1934).
[4] See remarks and reference, BS J. Research **2**, 916 (1929) RP64.
[5] This work on the properties of water is appearing in the Monograph Series of the American Chemical Society.

the NBS formula beyond the range of the observations. Such extrapolation is justified by the desirability of using a consistently continuous reference line for all the observations, and is not to be inter-

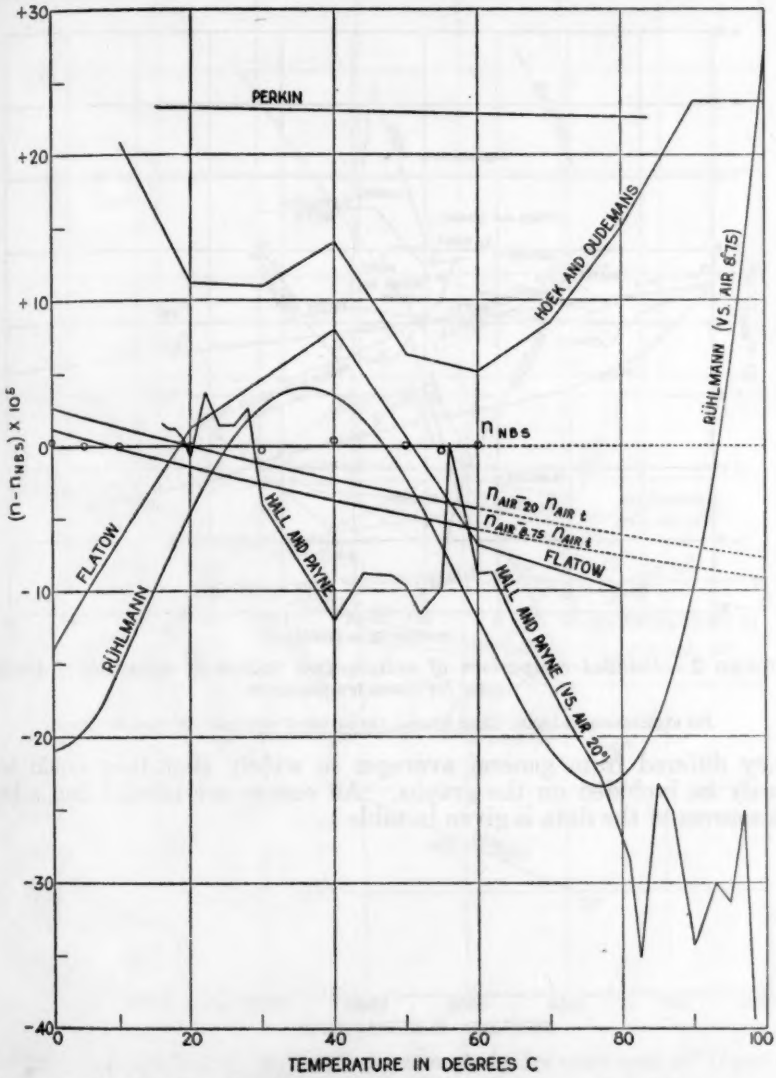

FIGURE 1.—*Comparison of sodium-lines indices of refraction of distilled water over long temperature ranges.*

The line $\Delta n=(n-n_{NBS})\times 10^5=0$ represents the relative (to air at $t°$ C) index of refraction as computed by the general interpolation formula (see eq 3). Nine circles show the agreement between observed and computed values. Dotted lines indicate extrapolation. Corresponding computed indices relative to air at 20° and at 8.75° C, also indices published by other observers, have been compared with the NBS values by subtracting the latter from all others. Broken lines connect experimentally determined points and the continuous curve for Rühlmann is computed from the equivalent of his formula for index referred to air at 8.75° C.

preted as an indication that one should attach great importance to the formula beyond the experimental range from which it was derived.

In preparing these comparative exhibits an attempt was made to exclude all data taken with commercial refractometers and all data that for any other reason seem to rest on mere comparison bases. Values absolutely determined were not consciously omitted unless

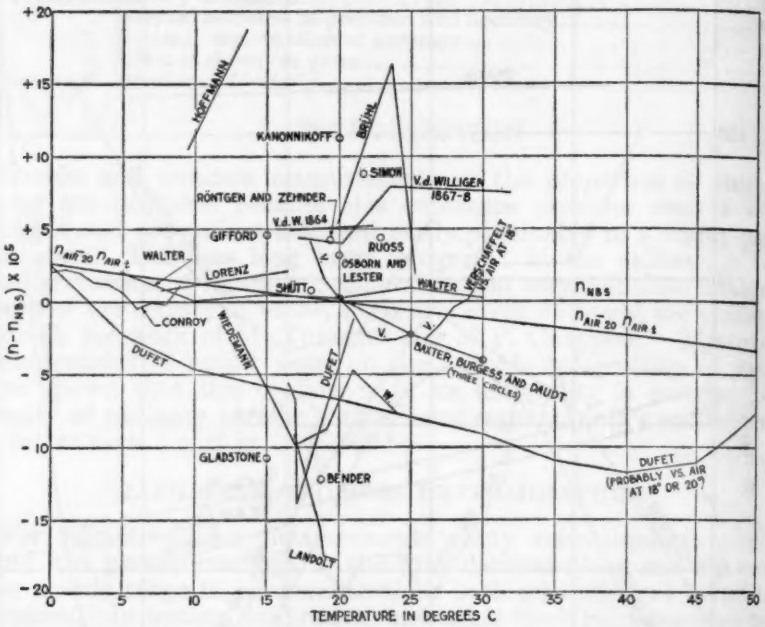

FIGURE 2.—*Detailed comparison of sodium-lines indices of refraction of distilled water for room temperature.*

For explanation see legend under figure 1, the curves of which are not reproduced here.

they differed from general averages so widely that they could not easily be included on the graphs. All curves are labeled and a key to sources of the data is given in table 1.

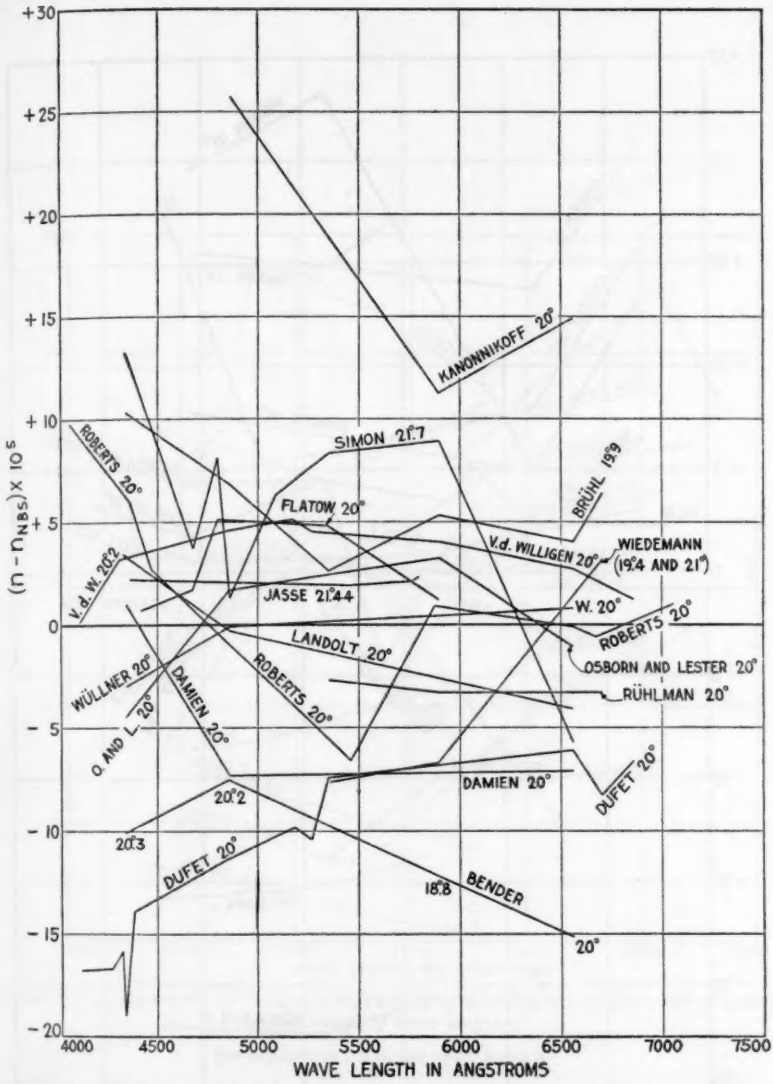

FIGURE 3.—*Comparison of indices of refraction of distilled water near 20° C over the visible range of wave lengths.*

The line $\Delta n=(n-n_{NBS})\times 10^5=0$ represents the relative (to air at t° C) index of refraction at any temperature, t, as computed by the general interpolation formula (see eq 3). Indices published by other observers have been compared with the NBS values (for identical temperatures) by subtracting the latter from all others. Broken lines connect experimentally determined points.

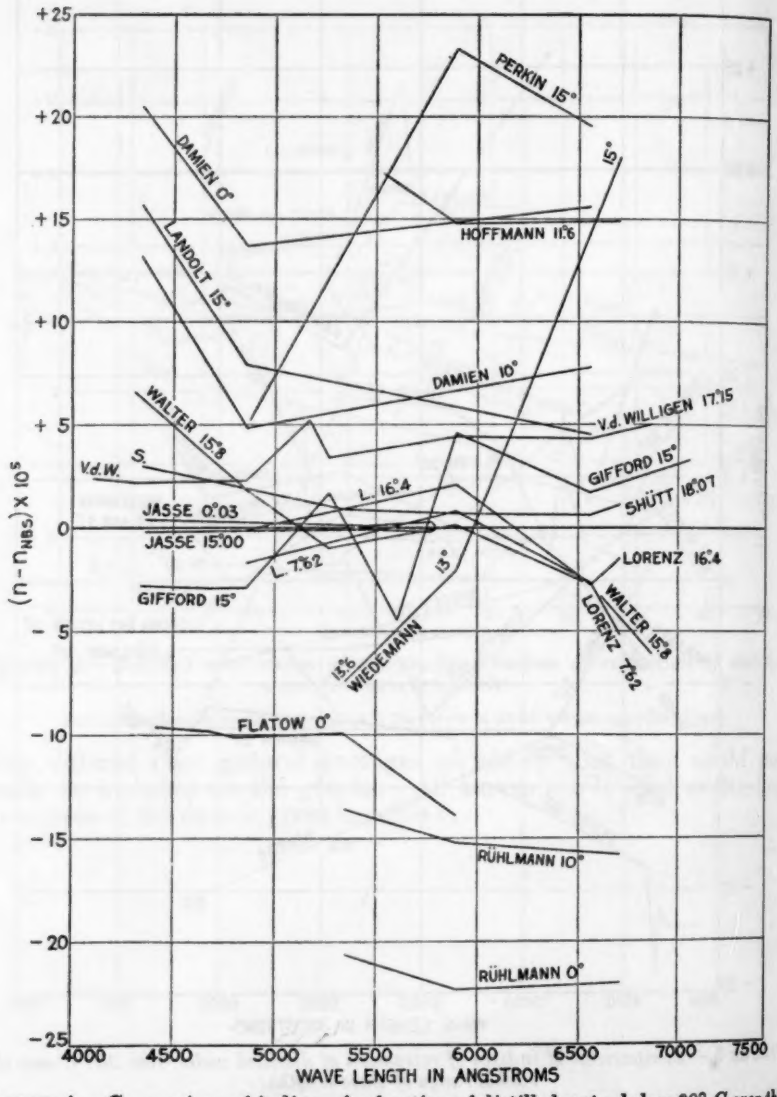

FIGURE 4.—*Comparison of indices of refraction of distilled water below 20° C over the visible range of wave lengths.*

For explanation see legend under figure 3.

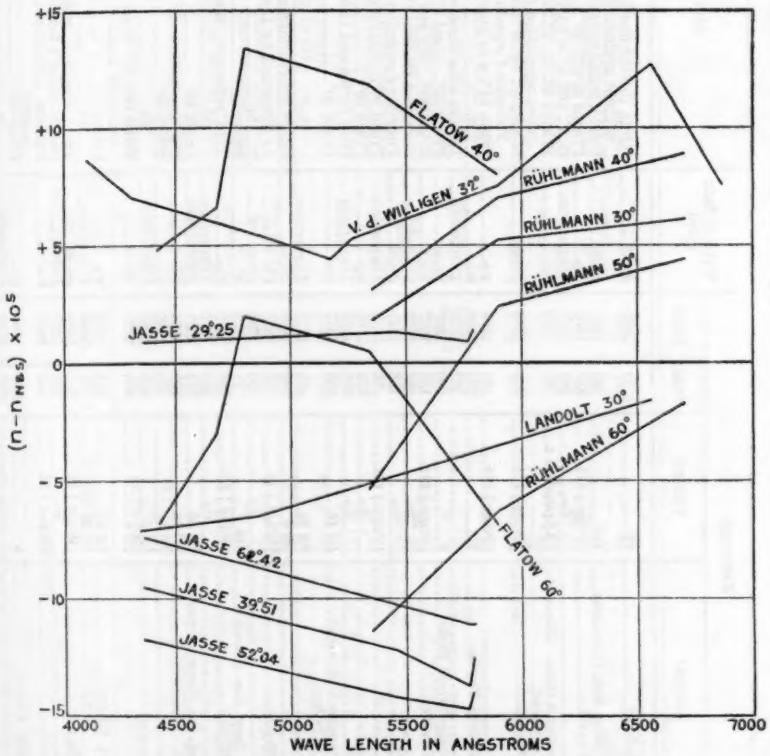

FIGURE 5.—*Comparison of indices of refraction of distilled water above 20° C over the visible range of wave lengths.*

For explanation see legend under figure 3.

TABLE 1.—*Key to data used for comparative exhibits in figures 1, 2, 3, 4, 5, 6, 12, and 13*

Investigator	Reference				Type of data cited	Method; and remarks	Figure No.
	Journal	Volume	Page	Date			
J. Jamin	Compt. rend	**43**	1193	1856	dn/dt	Jamin interferometer. Gives n as function of t without evaluation of n_0.	6
T. P. Dale and J. H. Gladstone	Trans. Roy. Soc. (London)	**148**	889	1858	dn/dt	Used a single orientation of prism.	6
H. Landolt	Ann. Physik	[Pogg.] **117**	359	1862	n_D	Prisms 50 and 60°	2
Do	do	do	361	1862	Dispersion	C, F, and G' of hydrogen	3, 4, 5
M. Hoek and A. C. Oudemans	Recherches Astron. Observatoire Utrecht.	(Appendix) **1**	62	1864	n_D	Prisms 56, 65, 75, and 88°. Symmetrical apertures; repetitions (Bessel's).	1
A. Müttrich	Ann. Physik	[Pogg.] **121**	429	1864	dn/dt	Measured optic axes of immersed aragonite. Function-t equation differentiated.	6
V. S. M. Van der Willigen	do	[Pogg.] **122**	191	1864	n_D	Prism 34°; n as function of t	2
Do	Arch. Musée Teyler	**2**	202	1869	n_D	do	2
Do	do	**2**	202	1869	Dispersion	Twelve solar lines; n as function λ	3, 4, 5
M. F. Fouqué	Ann. observatoire Paris	**9**	196	1867	dn/dt	Prism 60°. Used C, F, and G' lines also	6
R. Rühlmann	Ann. Physik	[Pogg.] **132**	186	1867	n_D	Prism 59°. Air at 7° R	1
Do	do	do	186	1867	Dispersion	Corrected to air at t°	3, 4, 5
Do	do	do	186	1867	dn/dt	Function-t equation differentiated	6
A. Wüllner	do	[Pogg.] **133**	16	1868	Dispersion	Prism 60°. Sixth-decimal data	3
K. Hoffmann	do	do	605	1868	n_D	Prism 60°	2
Do	do	do	605	1868	Dispersion	Data for 9.6 and 11.6° C averaged	4
L. Lorenz	Kgl. Danske Videnskab. Selskab, Skrifter.	[5] **10**	504	1875	n_D	Prism 60°	2
Do	do	[5] **10**	504	1875	Dispersion	do	4
Do	do	[5] 8	220	1869	dn/dt	Jamin interferometer. Lorenz' equation used	6
Do	Ann. Physik	[Wied.] **11**	84	1880	t of n_{max}	As computed by Lorenz	12
Do	do	do	100	1880	Spec. ref	do	13
J. H. Gladstone	Trans. Roy. Soc. (London)	**160**	11	1870	n_D	Prism	2
E. Wiedemann	Ann. Physik	[Pogg.] **158**	380	1876	n_D	Total reflection; immersed air	2
Do	do	do	380	1876	Dispersion	do	3, 4
B. C. Damien	Ann. sci. Éc. Norm. super	[2] **10**	275	1881	Dispersion	Prism 60°	3, 4
Do	J. phys	[1] **10**	200	1881	t of n_{max}	Undercooled to −8° C	(12)
H. Dufet	do	[2] **4**	392	1885	n_D	Prism 90°	2
Do	do	[2] **4**	394	1885	Dispersion	do	3
Do	do	[2] **4**	403	1885	dn/dt	Prisms 90, 45°; immersed quartz, glass. As computed by Dufet.	6
J. Kanonnikoff	J. prakt. Chem	[2] 31	352	1885	n_D	Prism	2
Do	do	[2] 31	352	1885	Dispersion	do	3
E. Ketteler	Ann. Physik	[Wied.] **33**	515	1888	dn/dt	Total reflection; immersed air	6
Do	do	do	516	1888	t of n_{max}	(See Ketteler's footnote 2)	12
C. Pulfrich	do	[Wied.] **34**	332	1888	t of n_{max}	Pulfrich refractometer. (See footnote 31, this paper.)	12
F. Schütt	Z. physik. Chem	**5**	358	1890	n_D	Prism 60°	2
De	do	**5**	358	1890	Dispersion	do	4

TABLE 1.—*Key to data used for comparative exhibits in figures 1, 2, 3, 4, 5, 6, 12, and 13*—Continued

TABLE 1.—*Key to data used for comparative exhibits in figures 1, 2, 3, 4, 5, 6, 12, and 13*—Continued

Investigator	Reference				Type of data cited	Method; and remarks	Figure No.
	Journal	Volume	Page	Date			
C. Bender	Ann. Physik	[Wied.] 39	90	1890	n_D	Prism 60°	2
Do	do	do	90	1890	Dispersion	do	3
W. C. Röntgen and L. Zehnder	do	[Wied.] 44	48	1891	n_D	Prism 60°	2
J. W. Brühl	Ber. deut. chem. Ges	24	648	1891	n_D	Prism	2
Do	do	24	648	1891	Dispersion	do	3
B. Walter	Dissertation, Hamburg		31	1891	n_D	Prisms 63 and 84°; "Umkreisungsverfahren"	2
Do	Ann. Physik	[Wied.] 46	424	1892	Dispersion	do	4
Do	do	do	424	1892	dn/dt	Function-t equation differentiated	6
W. H. Perkin	J. Chem. Soc	61	292	1892	n_D	Prism 60°; elaborate prism housing	1
Do	do	61	292	1892	Dispersion	do	4
H. Ruoss	Ann. Physik	[Wied.] 48	535	1893	n_D	Telescope, scale, mirror half immersed	2
J. Verschaffelt	Bul. acad. roy. Belg	[3] 27	71	1894	n_D	Prism 60°; data at 23 temp; (least squares)	2
H. Th. Simon	Ann. Physik	[Wied.] 53	556	1894	n_D	Prism 30°; normal incidence	2
Do	do	do	556	1894	Dispersion	do	3
John Conroy	Proc. Roy. Soc. (London)	[A] 58	232	1895	n_D	Prism 60°	2
Do	do	[A] 58	232	1895	t of n_{max}	Differentiation of equation fitted by the authors	12
E. Flatow	Dissertation, Berlin		21	1903	n_D	Marten's 30° quartz twin prisms	1
Do	Ann. Physik	[4] 12	91	1903	Dispersion	do	3, 4, 5
Do	do	[4] 12	95	1903	Spec. ref	(Flatow's 20° value corrected)	13
Do	Int. Critical Tables	7	13	1930	dn/dt	Differentiation of (Martens'?) equation	6
J. W. Gifford	Proc. Roy. Soc. (London)	[A] 78	408	1906–7	n_D	Prism	2
Do	do	[A] 78	408	1906–7	Dispersion	do	4
G. P. Baxter, L. L. Burgess, and H. W. Daudt.	J. Am. Chem. Soc	33	901	1911	n_D	Prism 60°; elaborate prism housing	2
Do	do	33	901	1911	Spec. ref	do	13
F. A. Osborn and H. H. Lester	Phys. Rev	35	216	1912	n_D	Spectrometer and immersed grating	2
Do	do	35	216	1912	Dispersion	do	3
F. A. Osborn	do	[2] 1	208	1913	dn/dt	Abbe-Pulfrich interferometer; λ=5461 A	6
E. E. Hall and A. R. Payne	do	[2] 20	253	1922	n_D	Prisms 60 and 75°; elaborate prism housing	1
Do	do	[2] 20	255	1922	dn/dt	Function-t equation differentiated	6
R. W. Roberts	Phil. Mag	[7] 9	378	1930	Dispersion	Martens' method; 30° hollow prism	3
Nora Gregg-Wilson and Rob't. Wright	J. Phys. Chem	35	3013	1931	t of n_{max}	Immersion refractometer	12
O. Jasse	Compt. rend	198	163	1934	Dispersion	Interference; 4 wave lengths	3, 4, 5

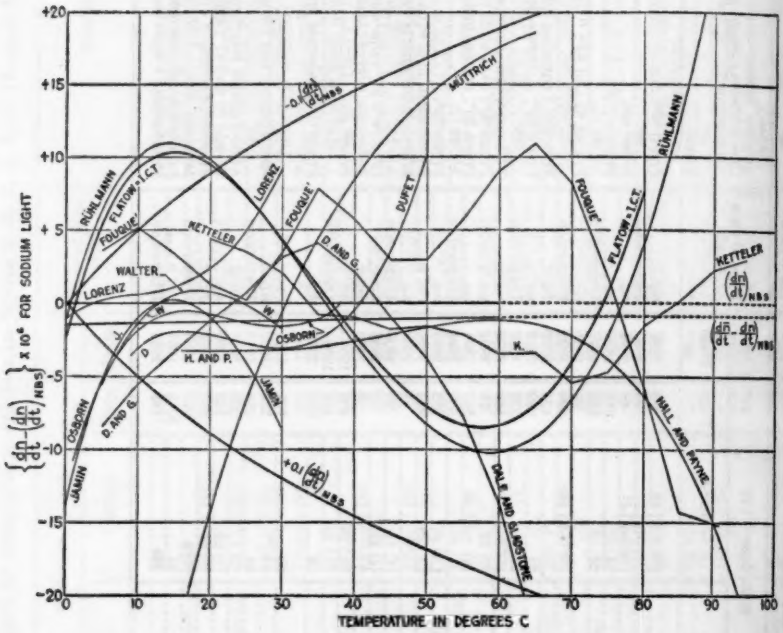

FIGURE 6.—*Comparison of various reported temperature coefficients of the refractive index of distilled water.*

The line $\Delta\frac{dn}{dt}=\left\{\frac{dn}{dt}-\left(\frac{dn}{dt}\right)_{NBS}\right\}\times 10^6=0$ represents the coefficient of relative index as computed from approved index data (see eq 5). Dotted lines indicate extrapolation. Corresponding computed coefficients of absolute index, $d\bar{n}/dt$, also coefficients published by other observers, have been compared with the NBS coefficients of relative index by subtracting the latter from all others. All data excepting Osborn's refer to the sodium lines. Heavy lines in the upper and lower portions of this figure show, respectively, the loci corresponding to minus and plus 10 percent deviation from the NBS temperature coefficient of relative index.

In preparing figures 1 to 5, discrete experimental indices as given by previous observers were used in preference to computed values, except in the case of Rühlmann, whose data are so numerous and imprecise that confusion was avoided in figure 1 by using his formula instead of his individual determinations. Flatow's values of index should be especially noticed because they have been much used and because a formula published in the International Critical Tables is exactly equivalent to one computed (perhaps by Martens) to fit closely Flatow's data for the *D* lines of sodium.

On the other hand, in preparing figure 6, showing the derivatives of the index with respect to the temperature, formulas were preferred to the use of finite differences, except only in the case of the three broken lines which connect temperature coefficients computed by differences. Here the Fouqué data were examined numerically and the coefficients thus deduced were found to differ appreciably from those given by Dufet as the result of his graphical solution. Likewise, the curves drawn here for Rühlmann and for Müttrich are somewhat different from those obtainable from Dufet's tabulated values; probably because Dufet seemingly ignored their published index equations. For the Dale and Gladstone data the temperature coefficients deduced by the present writers are in fair agreement with data listed by Dufet for those investigators. Flatow's curve in figure 6 was computed by use of the formula that fits Flatow's index observations. This curve is drawn slightly prominent because it also represents data on the temperature coefficient of water as given in the International Critical Tables.

With exception of data on the *D* lines of sodium, the only extensive series of explicit values of dn/dt seems to be that published by Osborn for the mercury line $\lambda=5461$ A. Accordingly, the comparison of his data with the corresponding data of this paper for $\lambda=5461$ A is combined with the sodium-lines exhibit in figure 6.

Figures 1 and 2 show that even for the *D* lines of sodium it is impossible to select with confidence any value for the fifth decimal place of the refractive index. When other wave lengths are considered, as in figures 3, 4, and 5, it is apparent that the value of $(n-1)$ for water can not be considered as established with an accuracy much greater than 1 part in 1,000. Temperature coefficients of refractivity, some of which have been obtained by interferometric methods, also vary greatly, as shown in figure 6, where the limits of ± 10 percent variation are plainly indicated. All these comparative exhibits, figures 1 to 6, show the rather large spreads in numerical values that have been found by various investigators; and they emphasize the difficulties that seem to characterize precise refractive-index measurements.

II. DESCRIPTION OF APPARATUS

All refractive-index determinations reported here were made by the method of minimum deviation using a hollow prism, intimately water jacketed and immersed in a stirred air bath within a constant-temperature prism housing on the table of a spectrometer. All water temperatures were measured by specially designed platinum resistance thermometers.

1. SPECTROMETER

The spectrometer, figure 7, used in these determinations was made by the Société Genevoise and modified in this Bureau's instrument shop by removing the principal clamps and slow-motion screws and mounting the prism-table axis directly on the central cone of the instrument. The constant-temperature prism housing, the connections to the mixing chamber, and the circulatory system have been described in a previous paper.[6]

The collimator and telescope objectives are of 405-mm focal length. A rotatable eyepiece micrometer on the telescope permits rapid and accurate measurements on the pyramidal errors of prisms, and also provides for using a series of cross wires of various sizes and patterns when working with spectral lines of various intensities.[7] A number of eyepieces of focal lengths from 5 to 35 mm are provided, and one of the Gauss type is used for autocollimation and for making the usual adjustments with the aid of a plane-parallel plate.

A side-tube pseudo-collimator, essentially as described by Guild,[8] is used almost exclusively for routine leveling and for measuring prism angles. The leveling is, of course, often checked by using the Gaussian eyepiece.

(a) CIRCLE

The circle is 308 mm in diameter, and is graduated to 5-minute intervals. The errors of position of the degree graduations have not been explicitly investigated. Analyses of many index data indicate that such errors are approximately ± 1 second in magnitude, but in all refracting-angle measurements of importance these errors are practically eliminated by the method of repetitions, using different portions of the circle in proper sequence. In (double) minimum-deviation measurements the errors of graduation are somewhat less important and with proper circle orientations (see section III–4), they also are satisfactorily reduced by the numerous repetitions that must be made for other reasons.

Errors of subdivision of the degree intervals on this circle are fully as large as those of the degree graduations, and perhaps more important. The magnitudes and systematic trends of these errors were determined by measurements on a few degree intervals at widely separated positions around the circumference of the circle. Each of these degree intervals was measured, in turn, by each of four micrometer microscopes. These measurements show that there is a periodic error that repeats three times in each degree interval and has an amplitude of approximately 1.7 seconds, as shown in figure 8. This, presumably, was caused by a periodic error in the mechanism that controlled the degree-subdivision graduations when the circle was ruled. For two micrometer microscopes separated by exactly 180° the same correction would be required for each of them and for the average of their readings, but the periodic nature of these errors is such that by making the separation 179°50′ the correction to their averaged reading does not exceed $\pm 0.2''$, as is shown by the heavy line in figure 8.

---

[6] Leroy W. Tilton. J. Research NBS 17, 389–400 (1936) RP919.

[7] Most minimum deviations determined by the authors are made with wide collimator slits (in order to lessen "chromatic parallax") as described and recommended by Guild, Proc. Phys. Soc. (London) 29, 329 (1916–17); or Nat. Phys. Lab. Collected Researches 14, 265 (1920).

[8] Dictionary of Applied Physics 4, p. 115 (Macmillan & Co., Ltd., London, 1923).

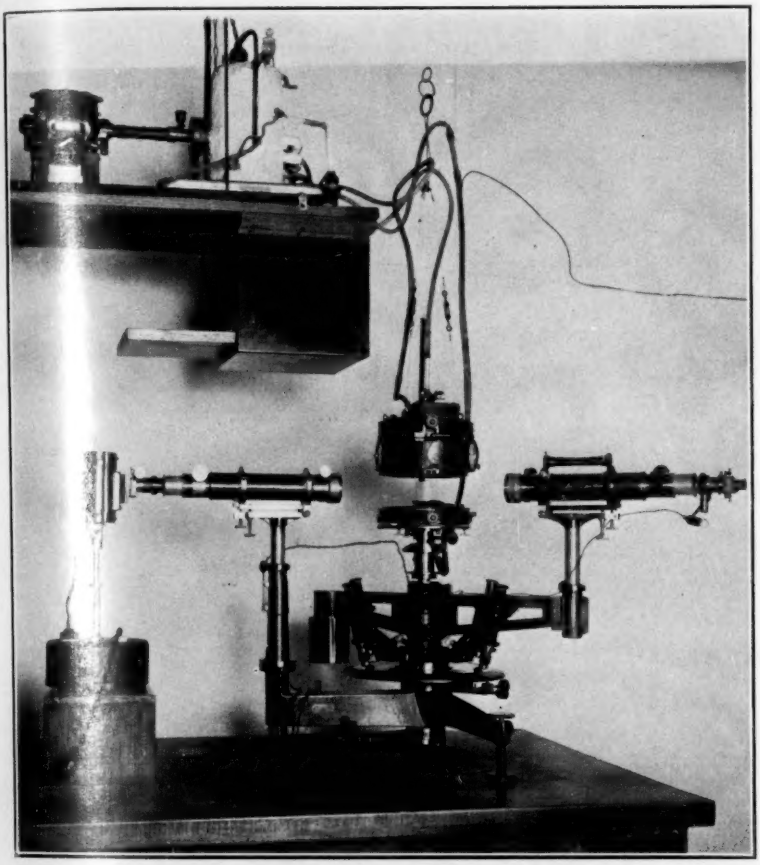

FIGURE 7.—*Spectrometer and auxiliary apparatus for temperature control.*

Motor, rotary pump, and conditioning chamber with thermoregulator are located on a shelf supported from wall and ceiling. The upper portion of the constant-temperature prism housing is shown suspended by wire, pulley, and counterweight a few inches above its working position. For refractometry of liquids a hollow-prism assembly replaces the glass prism on the spectrometer table.

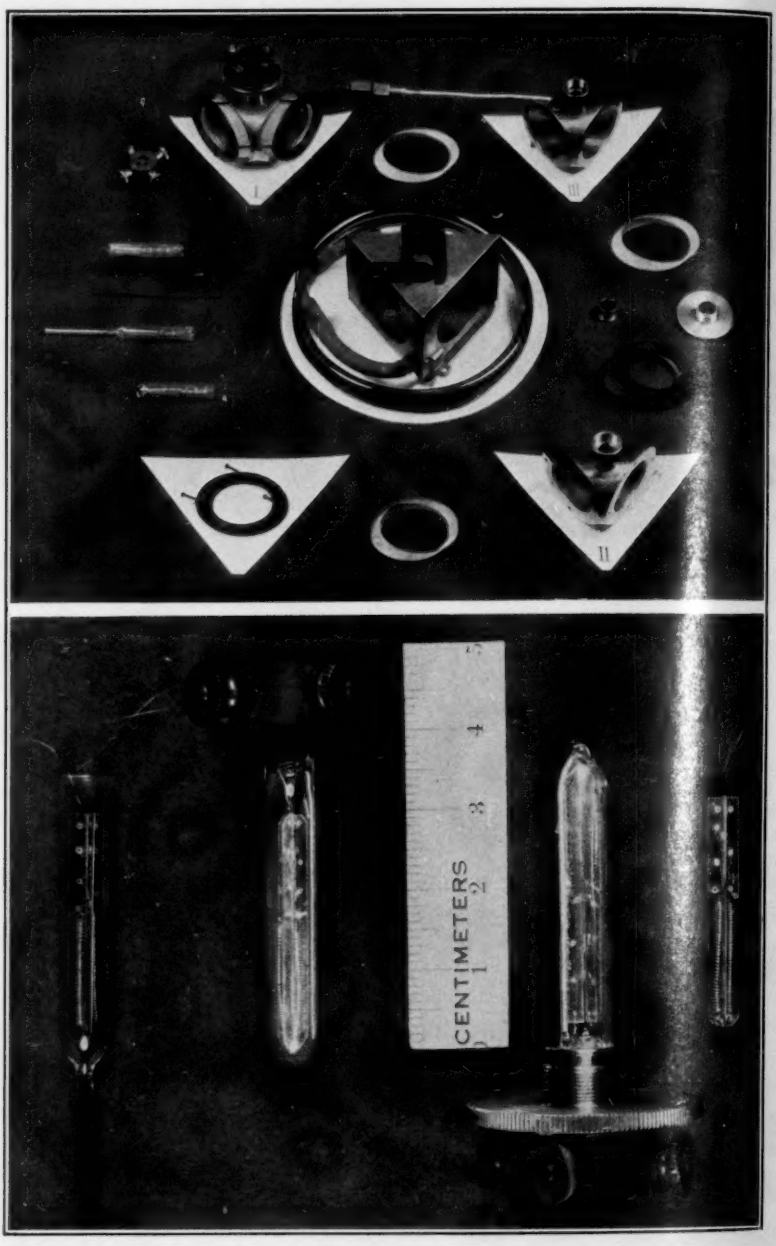

FIGURE 9.—*Hollow prisms, water jacket, and platinum resistance thermometers.*

In the center (top) is the prismatic water jacket; around it are shown prism *I* completely assembled and with thermometer in position, prisms *II* and *III* unassembled, a completed thermometer, and others in course of construction. The enlarged view shows the thermometers, both completed and in process with metric scale for dimensions.

(b) MICROSCOPES

The circle is read by four 60-power micrometer microscopes situated at approximately 90° intervals around the circle. A fifth microscope of lower power and larger field permits readings to the nearest graduation. The micrometer screws make one revolution per minute of arc and the drums are graduated to read seconds directly, and tenths by estimation.

Figure 8 is drawn for the ideal case in which the microscope tube lengths are perfectly adjusted to correspond with the actual performance of the micrometer screws in connection with this particular circle. In general, however, if x is the fraction of a perfect 5-minute interval which is to be measured and k is the run correction for a full 5-minute interval, then either kx or $k\ (x-1)$ is the correction to be applied, depending on the choice of scale divisions to which the measurements are referred. In one case there is right-hand (say positive) travel of the micrometer slide between the respective settings of each microscope corresponding to the first and second telescope pointings; in the other case the effective travel is reversed, and the final error is opposite in algebraic sign. To adjust k to negligibly

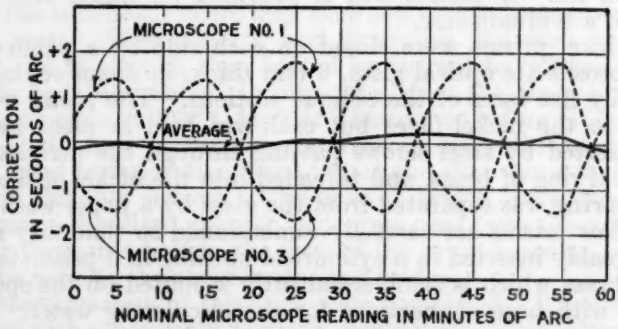

FIGURE 8.—*Elimination of positional error in degree subdivisions of the circle by use of microscopes 1 and 3.*

Correction of periodic error is automatically obtained by ±5′ displacements of two opposite micrometer microscopes. For microscopes 2 and 4 similar conditions exist.

small values, or even to determine k precisely is laborious. Moreover, it varies somewhat with the condition of the oil on the conical bearing and with adjustments of the friction in this bearing. Consequently, in all of these refractive-index determinations, k was merely kept small and the numbers $\overset{+}{N}$ and $\overset{-}{N}$ of the positive and negative runs were apportioned approximately in the ratio $|x-1|:x$ so that $\overset{+}{N}kx$, the sum of the corrections of one sign approximates $\overset{-}{N}k(x-1)$, the sum of the corrections of opposite sign. Consequently, for averaged angles no explicit correction for the run of the micrometers was necessary.

2. HOLLOW PRISMS OF NICKEL

The prisms used in these measurements on the refractivity of water were especially designed for the purpose. Each prism is a portion of a hollow cylinder of nickel, terminated by oblique sections cut at 54° with the cylinder axis so as to form an angle of 72° with each other. This angle of 72°, one-fifth of a circle, is an important feature of the design, because it permits approximately the maximum tolerance[9] in error of refracting-angle measurement, and because the average of five repetitions with proper circle orientation is a value for the refracting angle that is entirely free from errors of graduation of the circle. Moreover, for a prism with this angle the double minimum deviations for water are angles of approximately 60°, and therefore are particularly favorable values for the elimination of scale error by three repetitions when using two reading microscopes.

Nickel was chosen for making these prisms because it was readily available, has suitable mechanical properties, and was thought to be satisfactory as a container for distilled water. The prism walls were made especially thick, 6 mm, so as to provide ample bearing surfaces for the windows. The clear aperture is 22 mm in diameter and the capacity 10 ml. A central well is provided for filling and for the insertion of a thermometer.

These nickel prisms were closed on each side by a plane-parallel plate of borosilicate optical glass, 6 mm thick, in direct contact with the optically flat faces of the oblique sections. The plates were not cemented to the nickel faces but each was held in place by gentle pressure exerted by steel screws passing through the periphery of a flat elliptical ring of brass, and threaded into the nickel of the prism. Each brass ring was separated from the glass by a paper washer.

The hollow prisms are carefully dimensioned so that they may be interchangeably inserted in a cylindrical opening in a prismatic water jacket of brass which is semipermanently mounted on the spectrometer table with hose connections for the circulating water. A thin film of vaseline is used to reduce friction and improve thermal conductivity between the prism and its brass water jacket. The interchangeable feature permits convenient and rapid removal of the prism for refillings, without breaking the hose connections and without seriously disturbing the thermostatic adjustment.

Three hollow prisms of this general type have been used extensively in these determinations. They are shown in figure 9 with the brass water jacket in which they are used. Prism *I*, used almost exclusively in the approved series of measurements, is essentially as described above. Prism *II*, almost identical with *I*, but chromium plated on its interior surfaces, was used alternately with *I* in many preliminary measurements on dispersion of water[10] at 20° C. The general average of indices determined with prism *II* exceeded the average with prism *I* by 6×10^{-7}, but this was almost entirely the result of relatively imprecise data for the very faint helium line $\lambda=4026$ A. For the 24 other wave lengths used in this preliminary work the average difference was 1×10^{-7} in index. Apparently, then, nickel and chromium are equally serviceable for such work.

[9] See figure 1 on p. 921 of BS J. Research **2**, 916 (1929) RP64.
[10] Leroy W. Tilton. J. Research NBS 17, 639-650 (1936) RP934.

A special prism, *III*, for use in auxiliary determinations of the index in vacuo, was provided with a silver thermometer well, an auxiliary capillary tube of silver for filling, and in this case the windows were cemented to the nickel faces, at times with Duco, a cellulose nitrate material, and again with beeswax.

3. PLATINUM RESISTANCE THERMOMETERS

Small platinum resistance thermometers of the potential-terminal type were made for these experiments and used with a Leeds and Northrup precision thermometer bridge and commutator. Wire 0.05 mm in diameter was annealed and wound on a mandrel (1.7 mm in diameter) to make a 25-ohm coil with a fundamental interval of 10 ohms. This coil was bent into four equal portions which were mounted on a mica cross and inserted in a glass tube in such manner that each quarter of the coil occupied a dihedral angle of 90°. The exterior diameter of the tube was 6 mm and the sensitive or bulb portion was 15 mm in length. Extra leads of the same wire were arc-welded to each end of the coil proper and all leads were threaded through mica for approximately 15 mm. Leads of 0.1-mm platinum wire were used from the top of the mica through the glass seal and into the Bakelite head, where they were soldered to the copper terminal binding posts. After winding and mounting, the wire was washed in water and in alcohol, then heated by current to redness, and after the leads had been sealed through the glass the thermometer was heated in an oven at 200° C for 2 or 3 hours just before filling with dry hydrogen. Copper binding posts were securely threaded into the Bakelite head (exterior diameter 15 mm) and that was attached to the glass with Bakelite cement. The over-all length, including the head, was 54 mm. Standard exterior leads were used from the copper binding posts through a hole in the floor of the prism housing, and thence across the room to the commutator and bridge.

Two thermometers of this type were completed. They are shown in figure 9 with others only partially completed. These thermometers were calibrated by the thermometer section of this Bureau, and the constants are listed in table 2.

The Callendar δ was determined by comparison with a standardized platinum resistance thermometer at approximately 30° C. For thermometer designated as 2, an additional delta determination at approximately 50° gave a value of 1.61, which indicates satisfactory constancy over this range. This δ value is, however, considerably higher than would ordinarily be expected for platinum of the purity indicated by the slightly low value of $(R_{100}-R_0)/R_0$, namely, 0.386, which is found in this case, instead of 0.392 as is found for pure platinum. This platinum was known to be of high purity when in the form of wire 0.4 mm in diameter, and soon after it had been drawn to 0.05 mm diameter by a manufacturer of platinum ware it was sampled at one end and found to have a nearly normal value of $(R_{100}-R_0)/R_0$. Much later, after the completion of these thermometers, further tests along the length of the wire showed progressively increasing contamination. Evidently the existing contamination is different in kind from that ordinarily encountered and the usual inferences relating to values of the fundamental coefficient and of δ are not necessarily applicable.

TABLE 2.—*Constants of resistance thermometers*

Thermometer (number)	Resistance, R_0, in melting ice	Fundamental interval	δ of the Callendar formula
1	25.307$_8$	9.740$_4$	1.62$_4$
2	25.732$_4$	9.945$_4$	1.62$_4$

Irrespective of the particular degree or kind of existing impurity, the calibration data show that the observed values of resistance at 0, 30, 50, and 100° on the international temperature scale can be reproduced by the Callendar equations which have three adjustable constants. Therefore, the temperatures as determined with these thermometers, especially in the range used (0 to 60° C) may be considered sufficiently accurate even though the value of the constant δ is somewhat unusual.

Since these thermometers were not designed or used for temperatures above 100° C, and since when in use the head and the coil were always at the same temperature within a few tenths of 1° C, the use of short leads is permissible. Ice-point determinations indicate that R_0 decreased about 0.000$_3$ ohm over a period of 6 years. Individual ice point determinations vary somewhat erratically by $\pm$0.000$_2$ ohm and this is attributed to variable strain in portions of the coils that are not adequately supported by mica. Fortunately, this variation is equivalent to only $\pm$0.002° C and therefore is unimportant for the refractometry of water.

4. THERMOMETER BRIDGE

A precision thermometer bridge of the 5-dial Mueller type, balanced by the null method, was used with a high-sensitivity galvanometer. The effects of lead resistance were completely eliminated by means of a commutator. Each step of the last dial on the bridge corresponds to about 0.001° C and to a deflection of about 1 mm on the scale, with a current of 2.5 milliamperes in the 25-ohm thermometer.

Since for refractometry, expecially of water, an accuracy of $\pm$0.003° C ($\backsimeq$ 0.0003 ohm approximately) seemed ample, it was decided to insulate the bridge thermally rather than to build an apparatus to control its temperature. Consequently, the bridge, an auxiliary standard resistance of 25 ohms, and below the bridge a flat water-filled tank of copper that supplied ample heat capacity and also served as a unit of the electrical-shielding system were housed in a box of oak with double walls, each ½-inch thick, interlined with 2-inch cork. The oak box was provided with a lid through which all controls were extended to permit operation from the exterior.

The auxiliary 25-ohm resistance was carefully calibrated for temperatures from 20 to 30° C in the resistance measurements section of this Bureau, and the bridge was initially calibrated at 23.5° C by that section. Also, the 25-ohm resistance was checked at intervals thereafter and other calibrated coils were occasionally borrowed from the resistance measurements section for use in further checking the bridge performance. By such means certain coils of the bridge were calibrated, at different seasons of the year, for all existing room temperatures. Frequently, during index determinations, the 25-ohm standard

resistance was used to check the constancy of 25 ohms of the bridge resistance. Occasional ice-point determinations served to check the continued constancy of the thermometers.

At and near each temperature for which indices were to be measured, tables of bridge readings were prepared, with columns for different bridge-box temperatures. In this way it was possible to read and record each water temperature immediately after the resistances were recorded.

III. EXPERIMENTAL PROGRAM AND PROCEDURE

Although the use of water of highest possible purity would be desirable, previous experience had indicated that impurities in freshly distilled water influence refractivity much less than they do electrical conductivity or even density. Certainly, determinations should be made at so many temperatures and wave lengths that regularity over the refractive-index surface could be definitely established, but precise index determinations in this laboratory for 25 wave lengths had yielded no evidence of peculiar behavior, and published densities of water had not indicated irregularities in its expansivity.[11] Furthermore, great difficulties are involved in storing or keeping extremely pure water and much time is required for attaining temperature equilibrium and for the satisfactory elimination of certain errors by variations in experimental procedures. Such reasons governed the adoption of the program now to be outlined.

1. SAMPLING THE WATER

The distilled water used in these investigations was made from Washington city water by a Tripure still of 30-gallon-per-hour capacity, which is in daily service at two-thirds capacity to provide distilled water for the Chemistry Division of this Bureau. By means of a tap located in the line adjacent to the condenser, the hot distilled water was collected in a fused-quartz flask, of 125-ml capacity, which was immersed in a vessel containing cold water. Immediately afterward the flask was loosely covered with a small inverted beaker and carried to the refractometric laboratory where a sample of about 9 ml was transferred to the hollow prism, usually within 10 minutes after distillation. The transfer was made by means of a 10-ml pipette, which was thoroughly clean and used for this purpose only. The thermometer was washed in distilled water just before insertion and, to exclude further contact with air of the room, a nickel collar fitting the thermometer was finally screwed into the thermometer well.

Frequent routine measurements made by the Chemistry Division show that the specific conductance of this water at 20° C ordinarily ranged from 0.6 to 1.3×10^{-6} reciprocal ohm-centimeter. Samplings for index measurement were not made unless the still was thought to be in excellent working condition. On one sample a pH determination, made approximately 1 hour after sampling, gave a value of 6.1, which is about what should be expected for pure water nearly, but not fully, saturated with the atmosphere.

For almost all these approved index determinations this sampling of water was done on three different days so that the final results

[11] Leroy W. Tilton and John K. Taylor. J. Research NBS 18, 205-214 (1937) RP971.

are averages for complete measurements on each of three independent samplings.

In this connection, it may be mentioned that one complete measurement of index for the helium line 5876 A, made in January 1932, at the request of the late Dr. Edward W. Washburn, on a sample of redistilled normal water that he had prepared for the purpose, gave 1.332554_4 at 25° C as compared with 1.332554_8 which, at that time,[12] was considered a "best value" for samples from the still, thus confirming the purity of these samples.

2. SAMPLING THE INDEX SURFACE

Index determinations were made at 13 temperatures separated by 5° intervals within the range 0 to 60° C. The four light sources and 13 spectral lines listed in table 3 were used. By using all of these temperatures and wave lengths, the whole refractive-index surface would have been referred to a network of 169 points on the temperature—wave-length plane. This program for sampling the index surface at more or less regularly distributed points was, however, shortened to 133 sets of coordinates by limiting the work at 15, 25, 35, and 45° C to determinations for the four bright lines of helium.

TABLE 3.—*Light sources, spectral lines, and wave lengths*

Character of source	Designation of line	Wave length in air [1] at 18° C and 760 mm of Hg
Helium tube		0.7065188
Do		.6678149
Hydrogen tube	*C*	.6562708
Sodium arc	D_m [2]	.589263
Helium tube	*d*	.5875618
Mercury arc		.576960
Do	*e*	.5460740
Helium tube		.5015678
Hydrogen tube	*F*	.4861327
Helium tube		.4713143
Do		.4471477
Mercury arc	*g*	.4358342
Do	*h*	.4046563

[1] These wave lengths (international system) in air, expressed in microns, are used in all computations involved in the data of this paper (see J. Research NBS 17, 640 (1936) RP934).
[2] Hartmann's weighted mean for lines D_1 and D_2.

It was found advisable to limit the measurements of index to a single temperature on any one day, on account of the time required for establishing a particular temperature equilibrium throughout the sample. It was not difficult, however, for each of two observers, working alternately, to determine minimum deviations for about five spectral lines in a single day. Consequently, to minimize systematic errors, some high and some low temperatures were employed more or less alternately as the whole program advanced, and the spectral lines chosen for use on a given day were always well distributed over the spectral region. The choice of alternately high and low working temperatures was limited, however, by another consideration, namely, the advisability of reserving for winter the work at and near 0° C and for sum-

[12] It may be noticed that this measured index of Dr. Washburn's sample of redistilled water is lower than the corresponding entry in table 5 by 11×10^{-7}. However, this difference is small and involves not only accidental errors but possible secular changes in apparatus over a period of 1 or 2 years.

mer the determinations at and near 60° C. Since, however, the approved series of observations extended over the interval from May 11, 1931 to June 18, 1934, it was possible to proceed more or less in accord with each of these considerations.

3. REFRACTING-ANGLE MEASUREMENTS

The windows of the hollow prism are plane parallels within approximately one-fourth second of arc and, moreover, were paired in such manner that the error in deviation at the entrant window was offset by one of opposite sign at the emergent window. Consequently, the refracting angle of the prism of water can be assumed to be identical with the angle between the exterior surfaces of the windows. This angle was determined on each working day both before and after minimum-deviation measurements. At least 6 and usually 10 measurements of this angle were included in each determination, using in a systematic manner various arcs of the circular scale; and duplication of circle orientations was usually avoided during the two complete determinations for any one day. In order to minimize torsional errors of the cone, one-half of all refracting-angle measurements were made on the angle itself, and the others on its explement.[13] Always, of course, care was taken to use the objectives symmetrically, and only autocollimating methods were employed for refracting-angle measurements.[14]

In most cases the refracting-angle determination made after minimum-deviation measurements differed from the corresponding initial determination by less than 1 second and sometimes the refracting angles differed less than ± 1 second over periods of several working days. All refracting angles used in computing indices of refraction were linearly interpolated between the two daily determinations, on the basis of elapsed time.

Occasionally the windows were removed in order to rearrange them or to readjust the screws and rings that retained them. To detect distortions by pressure, the planeness of the windows in situ was sometimes tested by interference fringes, and at times the zero deviation of the empty prism was tested by double deviation observations.

4. MINIMUM-DEVIATION MEASUREMENTS

After completion of an initial refracting-angle determination, thermal equilibrium being usually well established, the prism was properly adjusted for deviation measurements, by means of the exterior controls of the prism-table ways.[15] These measurements were always made, in turn, by each of two observers. Since double deviation was always of the order of 60°, three measurements were included in each observer's determination, the circle being advanced 60° between measurements. Each observer used a different initial scale orientation; and for the other samples of water, on second and third days, still other orientations were systematically chosen. Thus the final-average deviation at any given temperature, t, and wave length, λ, as measured on 3 samples, involves the use of 18 different sets of scale rulings, all of which were symmetrically distributed on the circle.

[13] See BS J. Research **2**, 930 (1929) RP64.
[14] See BS J. Research **11**, 30 (1933) RP575.
[15] See BS J. Research **11**, 34 (1933) RP575.

To minimize, especially with respect to dispersion, the effects of possible errors that might progress with time, the two observers used the spectral lines in opposite sequences and the initial measurements on a given day were sometimes made on the shorter and sometimes on the longer wave lengths. Also, the observers often varied the daily sequence of their alternations between making the deviation and the temperature measurements.

5. TEMPERATURE CONTROL AND MEASUREMENT

During all measurements the temperature of the distilled water was controlled by a thermoregulator and a circulatory system, as described in a former paper.[16] A more or less continuous record of the experimental conditions was made by one of the observers. These records included readings of air temperature and humidity in the bath surrounding the hollow prism, barometer readings and temperatures, resistance readings and bridge-box temperatures, together with frequent entries of time and suitable designations of all deviations as they were being observed. By means of the double-entry tables mentioned in section II–4 the resistance measurements were immediately converted into temperatures.

The bridge was balanced between right and left telescope pointings during each minimum-deviation measurement, and thus for the completed program of triple sampling 18 temperature determinations are averaged for the final minimum deviation at any given t and λ. It was sometimes possible to make a full daily set of observations (say 24 measurements of deviation, 3 by each observer on each of 4 spectral lines) while the water temperatures remained constant within $\pm 0.002°$ C. The temperature level was so adjusted that the average of the observed temperatures seldom differed from the even values of 0, 5, 10, 15°, etc., by as much as 0.01° C.

In all cases temperatures were controlled for a preliminary period of at least 30 minutes during the initial adjustments and the refracting-angle determinations. Experience showed that very slight temperature changes were optically detectable by the accompanying defective imagery of the collimator slit as viewed through the telescope and prism. Care was exercised to measure deviations only when both the imagery and the resistance measurements had for several minutes continued to indicate satisfactory thermal conditions. Although the water sample was not stirred it should be remembered that the prism was intimately water-jacketed and, moreover, completely surrounded by stirred air having approximately the same temperature as the water.

IV. ADJUSTMENT OF OBSERVATIONS

Throughout these refractive-index measurements care has been taken to avoid, or at least to minimize, systematic error by proper choice of procedures, and to reduce accidental errors by a suitable number of repetitions at each individual step in the observational program. Several references to these matters have been made in this paper but for more complete discussion of many of them reference should be made to previous publications.[17]

[16] Leroy W. Tilton. J. Research NBS 17, 389-400 (1936) RP919. For observations at 0° C alcohol was added to the circulating water and brine was used around the cooling coils.

[17] See summary, J. Research NBS 14, 417 (1935) RP776.

It should be mentioned, however, that no correction has been made for error in prism orientation. From experience in this laboratory it is estimated that inaccuracies of orientation render the indices reported in this paper systematically high by perhaps 5 or 7×10^{-7}. On the other hand, when the empty prism was from time to time retested for zero deviation it was often found to give slight deviations toward its apex. These deviations were attributed to asymmetrical aberration caused by slight deformation of the window faces. Some slight changes of this nature in the glass windows may occur with time and during temperature changes, even under the very slight pressures to which the windows are initially subjected. As a result of these tests it was concluded that many of the measured indices were too low by a few units in the seventh decimal place. Since these negative errors are of the same small magnitude as the positive error arising from inaccuracy in orientation, it was decided to ignore them both.

1. REDUCTION TO STANDARD CONDITIONS

All indices reported in this paper for water at t°C were reduced to refer to dry air at 760 mm (Hg) pressure and at air temperature t by use of tables and procedures that have been described in detail in a former paper.[18] The ventilation of the laboratory was good during all index measurements; consequently, it is thought that the indices given refer to essentially normal air[19] at Washington during the period 1931–34.

The temperatures at which observations were made were so nearly the preselected values that approximate temperature coefficients of the index of water (as taken from preliminary work and from published data) were amply precise for correcting the observed indices to the preselected temperatures.

All determinations that were approved at the time of taking the observations have been included in the averages for final adjustment. In other words, no data have been rejected after computations were made.

2. CURVE FITTING

By least-squares adjustments, equations have been obtained for representing the observed indices in two complete and practically independent systems. The first of these, called the isothermally adjusted system, is merely a series of dispersion equations, one for each nominal temperature at which observations were made. The second system is in effect a general interpolation formula for the whole index surface within the limits of temperature and wave length used in these investigations.

(a) ISOTHERMALLY ADJUSTED SYSTEM OF DISPERSION EQUATIONS

The corrected indices of water for 13 wave lengths were independently adjusted for each of the temperatures 0, 5, 10, 20, 30, 40, 50, 55, and 60° C. This was done by least squares, and dispersion

[18] See paper cited in footnote 17.

[19] The CO_2 content of air must reach approximately 15 times the normal value in order to affect measured indices of water by 1×10^{-6}. See p. 402 of paper cited in footnote 17.

equations were used to express index, n, at each temperature, t, as a function of wave length, λ, in the form

$$n^2{}_t = a^2{}_t - k_t\lambda^2 + \frac{m_t}{\lambda^2 - l^2{}_t}, \quad (1)$$

which had been found to be particularly suitable for this purpose.[20] The indices for four wave lengths were similarly adjusted for each of the intermediate temperatures 15, 25, 35, and 45° C, excepting that the values for $l^2{}_t$ were determined by linear interpolation between the adjacent values found for the larger group. Obviously, less weight should be attached to the parameters for these four intermediate temperatures. All these parameters are given in table 4, and the variations of l^2 and of k are shown in figure 10. Those two

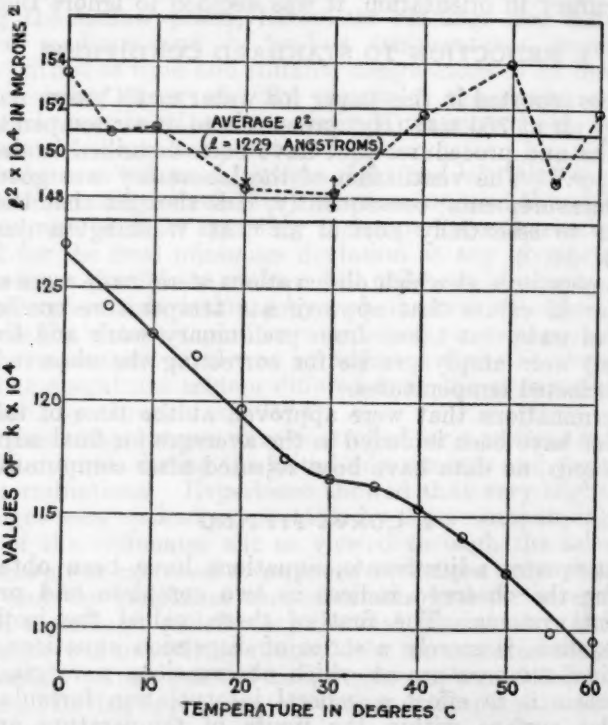

FIGURE 10.—*Dispersion parameters l^2 and k as functions of temperature.*

The cross at 20° C shows the value of l^2 obtained independently for many preliminary index data at 20° C. The arrows at 30° C indicate the estimated probable error in determinations of l^2.

are of special interest as their variations may represent shiftings of the effective absorption bands in the ultraviolet and the infrared, respectively. There is some difficulty in determining l^2 accurately,[21] but it is thought that the probable errors are not greater than is indicated by the arrows at 30° C in figure 10. It seems possible that the curve of l^2 has a minimum at or near 30° C, which would not be

[20] Tests were made with a series of indices of water determined at 20° C for each of 25 wave lengths. See J. Research NBS 17, 629–650 (1936) RP934.

[21] See discussion in J. Research NBS 17, 643 (1936) RP934.

surprising in view of prevailing ideas regarding the changes that take place in the association or structure of water as temperature is lowered (see section VI–4), but the evidence for a second minimum at 55° C is not convincing. Certainly, however, these data do not in general confirm the report by Flatow [22] to the effect that an increase of 1° C changes the ultraviolet resonance frequency by 0.3 A (that is changes $l^2\times10^4$ in microns squared, by 0.07) toward longer wave lengths. To the authors of this paper it seems probable that Flatow's values for the dispersion parameters may be seriously affected by the fact that he assumed a constant value for k and adjusted only the three others. Instead of a constant k the authors find values that, as shown in figure 10, decrease rather regularly as temperature rises, but indicate some change in trend at or near 30° C. The assumption of a constant value for l^2 instead of for k would seem a preferable procedure, and the unidirectional effect on resonance as temperature increases seems to be a shift in the effective infrared frequency to longer wave lengths.

TABLE 4.—*Isothermally adjusted values of dispersion parameters for eq 1*

[λ in microns]

t°C	a^2	k	m	l^2
0	1.7644735	0.0126866	0.00642337	0.0153533
5	1.7641459	.0124222	.00644785	.0150877
10	1.7636007	.0122994	.00644293	.0151148
15	1.7627786	.0121983	.00643914	(.0149759)
20	1.7616123	.0119672	.00644819	.0148370
25	1.7602512	.0117487	.00644524	(.0148306)
30	1.7587615	.0116583	.00643138	.0148242
35	1.7571550	.0116365	.00640079	(.0149996)
40	1.7553330	.0115298	.00637442	.0151750
45	1.7533297	.0114095	.00635272	(.0152896)
50	1.7511652	.0112507	.00633171	.0154043
55	1.7487297	.0109843	.00635168	.0148684
60	1.7464024	.0109516	.00630658	.0151833

(b) GENERAL INTERPOLATION FORMULA FOR THE INDEX SURFACE

In addition to representing the index of water as a function of λ, it is customary to express such values for any given λ as a function of t. The utilization of power series in t for this purpose has, in a former paper,[23] been discussed and compared with the use of the equation

$$(n_t-n_{20})_\lambda=-\frac{\overline{B}_\lambda(\Delta t)^3+\overline{A}_\lambda(\Delta t)^2+\overline{C}_\lambda\Delta t}{(t+\overline{D})\times10^7} \tag{2}$$

where $\overline{A}_\lambda$, $\overline{B}_\lambda$, and $\overline{C}_\lambda$ are functions of wave length, $\overline{D}$ is a constant, and $\Delta t=t-20$. For the D lines of sodium eq 2 was found to be more accurate than a power series having the same number of adjustable parameters. It was evident that, by successively using this function-t equation for each of the various wave lengths, determining the parameters independently in each case, a second or isofrequency system of function-t equations could be formed and the observations

[22] E. Flatow, Ann. Physik [4] 12, 93 (1903).
[23] Leroy W. Tilton and John K. Taylor. J. Research NBS 18, 205-214 (1937) RP971.

readjusted for comparison with the results previously obtained by isothermal adjustment. It seemed preferable, however, to combine both dispersion and function-t equations in a single function to represent the index surface over the observed range in the coordinates of temperature and of wave length.

In combining such dispersion and function-t systems it seemed advisable to consider the dispersion system as fundamental, because (1) its basic equation, which has been much used, rests more or less on theoretical grounds, and (2) the distribution of the observations was such that they sufficed for satisfactorily determining nine dispersion formulas whereas only four function-t formulas could be similarly adjusted and compared for as many as 13 observations each. It seemed permissible and convenient, also, to rely primarily on dispersions because (1) the dispersion system had already been completely adjusted and (2) the adjusted values of approved observations at 20° C were somewhat more numerous than those at other temperatures and, moreover, were supported by many preliminary observations at that temperature. Thus the dispersion equation for 20° C formed a very suitable "backbone" to which the other data could safely be referred during all initial adjustments of the proposed formula for the whole index surface.

By holding as constant the adjusted 20° data, and by using the whole isothermally adjusted dispersion system to compute "observed" data for the D lines of sodium, it was possible as described in a former paper [24] to determine tentatively by least squares four constants of the function-t formula for the sodium-lines index. More recently, by temporarily considering both 20° and D-line data as constant, it was found feasible, after a number of essays, to write six terms in λ and t and adjust by least squares the six additional parameters in such manner that all 133 observations were approximately represented by a general formula in λ and t with 14 tentatively adjusted constants.

There remained the necessity of either a complete least-squares readjustment of all 14 parameters using 133 observations or, alternatively, a continuation of step-by-step readjustments that would presumably be equivalent thereto, if continued. The latter procedure was adopted [25] and, first, all non-D-lines indices (except those for 20° C) were, by means of the six combined λ and t terms, reduced to D-lines equivalents. Then the 4 basic function-t constants, $\overline{A}$, $\overline{B}$, $\overline{C}$, and $\overline{D}$ were readjusted by least squares, using the 120 observational equations left after excluding the 20° C data. Second, all non-20° indices were reduced to 20° C equivalents by using the latest values for the constants in the whole function-t system, and then the four basic dispersion constants, a^2, k, m, and l^2 were readjusted, using 133 observational equations. The prospect of gains by further readjustments was not particularly good, but the importance of one

[24] J. Research NBS 18, 208 (1937) RP971.

[25] A step-by-step adjustment has distinct advantages over a complete single adjustment when one is concerned with several parameters and numerous observations, the curve fitting to have a precision of a few parts in 10,000,000. In initial stages of the progressive method, as used in this instance, the suitability in form of most of the various terms of the function is confirmed or disproved at comparatively early stages and the total extent of provisional computation is greatly reduced. Very definite confirmations of the general correctness of computational procedures are possible from time to time by summations of the squares of the residuals. It should be added that one is necessarily conscious of the relationship between additional readjustments and the betterments that they directly produce. Thus it is easier to limit computational effort at the proper degree of precision in adjustments without difficult and prolonged estimations made a priori.

of the combined λ and t terms appeared slight and the possibility of its satisfactory elimination seemed indicated. Accordingly, as a third and final step in these readjustments, all non-D and non-20° observations were used in readjusting the constants of the five remaining λ and t terms.

Thus there resulted a 13-constant formula which can, by using eq 1 and 2, be concisely represented by the equation

$$n_{(t,\lambda)}=n_{(20,\lambda)}+(n_t-n_{20})_\lambda \tag{3'}$$

provided it be further specified that three parameters of eq 2 are functions of λ as follows:

$$\left.\begin{aligned}\overline{A}_\lambda&=\overline{A}-a'\Delta\lambda\left(1+\frac{a''}{\lambda-l}\right)\\ \overline{B}_\lambda&=\overline{B}-\frac{b(\Delta\lambda)^3}{\lambda-l}\\ \overline{C}_\lambda&=\overline{C}-c\Delta\lambda\left(1+\frac{c'}{\lambda-l}\right),\end{aligned}\right\} \tag{4}$$

where $\Delta\lambda=\lambda-\lambda_D$, l is determined by the dispersion constant l^2, and a', a'', b, c, and c' are five arbitrary constants of what may be called the λ and t terms.

The 13 independent constants required for eq 3′ as a formula for the computation of refractive indices of water (wave lengths in microns, see table 3) are:

$a^2=$	1.7616316	20° C dispersion constants
$k=$	0.0119882	
$l^2=$	0.0149119 (l=0.1221145)	
$m=$	0.00644277	
$\overline{A}=$	2352.12	D-lines function-t constants
$\overline{B}=$	6.3649	
$\overline{C}=$	76087.9	
$\overline{D}=$	65.7081	
$a'=$	143.63	
$a''=$	0.4436	
$b=$	10.562	
$c=$	12504	
$c'=$	0.08430	

of which the first four are used in eq 1 to write a dispersion formula for 20° C, the second four are used in eq 2 to define temperature effects on the sodium-lines index, and the five that remain are used to express, according to eq 4, the effect of wave-length variations on the thermal behavior of refractive indices.

Equation 3′ as written in full is

$$n_{(t,\lambda)}=\left(a_{20}^2-k_{20}\lambda^2+\frac{m_{20}}{\lambda^2-l_{20}^2}\right)^{\frac{1}{2}}-\frac{\left\{\overline{B}-\frac{b(\Delta\lambda)^3}{\lambda-l}\right\}(\Delta t)^3+\left\{\overline{A}-a'\Delta\lambda\left(1+\frac{a''}{\lambda-l}\right)\right\}(\Delta t)^2+\left\{\overline{C}-c\Delta\lambda\left(1+\frac{c'}{\lambda-l}\right)\right\}\Delta t}{(t+\overline{D})\times 10^7} \tag{3}$$

and with proper substitution of the numerical values it becomes a general interpolation formula representing within a very few parts per million the refractive index of distilled water as determined by the authors for 133 pairs of temperature—wave-length coordinates. One-half of all residuals are within the limits ± 1, 80 percent are within ± 2, and 98 percent are within $\pm 3 \times 10^{-6}$ in refractive index. The average for all residuals is 1.2 and the maximum is 5×10^{-6}. The magnitude and distribution of these residuals are shown by circles in figure 11 where, also, the preliminary or isothermally adjusted system is represented by dotted lines. By comparing the dotted curves with the full straight lines, $\Delta n = 0$, it is apparent that the general temperature—wave-length system computed with 13 constants is closely equivalent to the isothermally adjusted system of indices computed by a series of 9 Ketteler-Helmholtz dispersion equations with a total of 36 constants.

V. RESULTS

By using the general interpolation formula (see eq 3) the index of refraction of distilled water was computed and tabulated in detail, the temperature of maximum index was determined as a function of wave length, and certain specific refractivities and partial dispersions were evaluated.

1. ADJUSTED VALUES OF INDEX OF REFRACTION

Table 5 gives, for temperature intervals of 0.5° C, the indices for each of the spectral lines that were used in this series of experiments. Values at 2.5° intervals were directly computed and the others were obtained by systematic interpolation to fifths.[26] The symmetrical distribution of the actual observations is shown by the use of boldfaced type at those points.

Since indices for the mean of the sodium lines are used much more frequently than others, calculations were made directly in this case for each 0.5° interval, and then, after interpolation to fifths, table 6 was prepared.

There remained the necessity of providing a general table from which the indices for all other wave lengths could be readily obtained. For this purpose direct calculations of index were made by the general formula (see eq 3) for each degree, and for values of λ in steps of 100 A from 4000 to 7200 A. Then, for each degree, interpolations for intermediate values of λ were made, by interpolation to fifths from 4000 to 5500 A and to halves from 5500 to 7200 A. These data are listed in the double-entry table 7. The tabular intervals of temperature and of wave length are so chosen that one may obtain sixth-decimal-place indices, by linear interpolation, almost as accurately as they can be computed. For temperatures below 10° C, however, the errors of linear interpolation may be as large as 7×10^{-7} in extreme cases.[27]

[26] See, for example, p. 89 of Theory and Practice of Interpolation by H. L. Rice, The Nichols Press, Lynn, Mass. (1899).

[27] No further reduction of such errors seems justifiable for the temperatures mentioned, because there are reasons for suspecting that all tabulated values of index may be relatively low by perhaps 1×10^{-6} at and near 0 and 5° C. At 0° C approximately one-tenth and at 5° one-twentieth of all "approved" observations were, through pressure of circumstances, made on water that had remained in the hollow prism for 24 hours longer than usual. Test data of this sort at 20° had indicated that the error of such procedure would be negligible. However, reference to figure 19 in section VI-4 enables one, by using the weighting factors just mentioned, namely, one-tenth and one-twentieth, to estimate that errors of -7 and -2×10^{-7}, respectively, may have been introduced in the averaged indices for temperatures of 0 and 5° C. Indices recently interpolated from table 5 for $\lambda = 5875.6$ A and temperatures between 3.4 and 4.0 ° C averaged 2×10^{-6} lower than certain values actually obtained late in March of 1933 by a few check measurements in that temperature range.

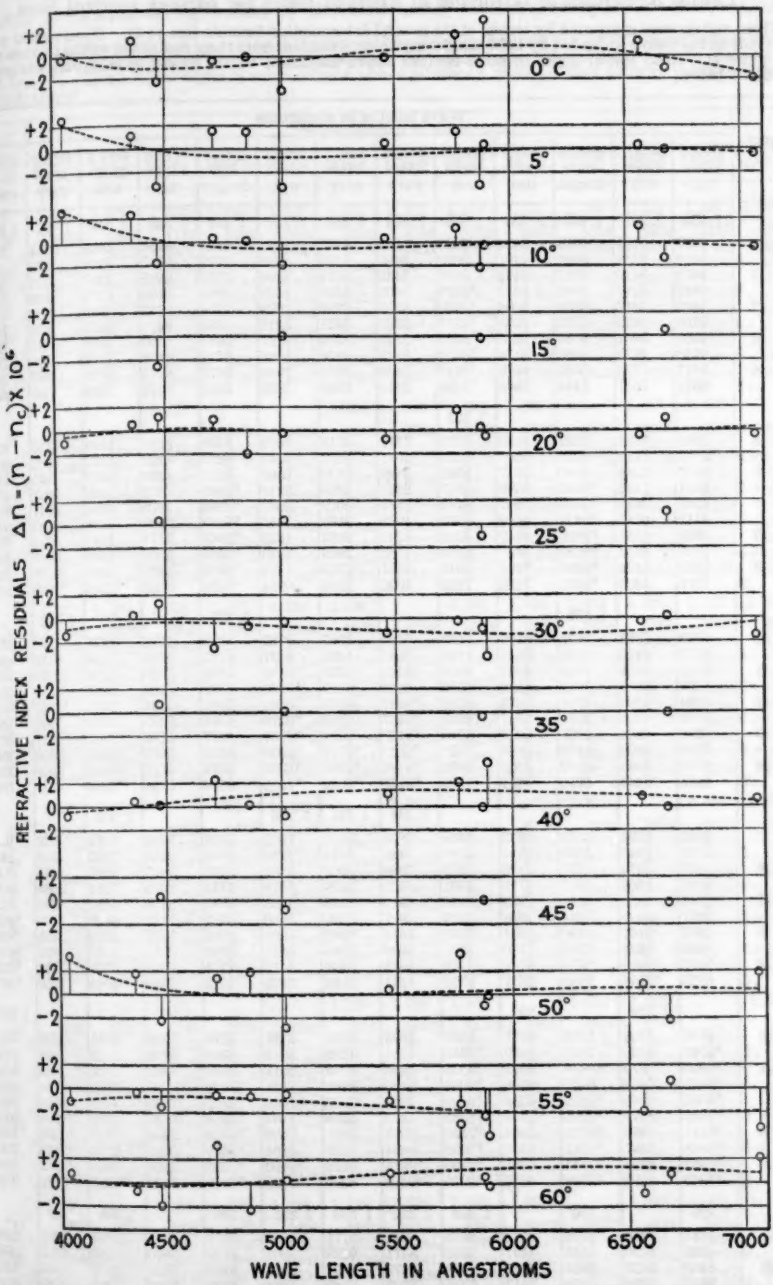

FIGURE 11.—*Deviations of the observed refractive indices of distilled water (circles for $n_o - n_c$) and of their isothermally adjusted values (dotted lines for $n_o - n_c$) from values, n_c, computed by the general interpolation formula (see eq 3).*

Of all residuals, $\Delta n = (n_o - n_c)$, 80 percent are within $\pm 2 \times 10^{-6}$, 50 percent are within $\pm 1 \times 10^{-6}$, and the average residual is 1.2×10^{-6}.

TABLE 5.—*Index of refraction of distilled water for various spectral lines*

[These values were computed by means of the general interpolation formula (see eq 3). Observations were made at the points indicated by bold-faced type; their deviations from these computed values are shown in figure 11. Read initial digits in same column above tabulated values unless asterisk refers to initial digits below]

t°C	Wave lengths in angstroms												
	7065.2 Helium	6678.1 Helium	6562.8 Hydrogen	5892.6 Sodium	5875.6 Helium	5769.6 Mercury	5460.7 Mercury	5015.7 Helium	4861.3 Hydrogen	4713.1 Helium	4471.5 Helium	4358.3 Mercury	4046.6 Mercury
	1.330	1.331	1.332	1.333	1.334	1.334	1.335	1.337	1.338	1.338	1.340	1.341	1.343
0	9477	8155	0939	9493	0028	3453	4397	3391	1129	9254	4248	2144	7564
.5	9482	8158	0940	9491	0026	3450	4393	3385	1122	9247	4240	2135	7553
1	9472	8145	0927	9474	0010	3433	4374	3364	1101	9225	4217	2112	7528
.5	9447	8118	0900	9443	*9978	3401	4341	3329	106	9188	4179	2073	7488
2	9409	8077	0858	9398	*9933	3355	4293	3279	1014	9137	4126	2020	7433
.5	9356	8022	0802	9338	*9873	3295	4231	3215	0950	9071	4059	1953	7364
3	9290	7954	0733	9265	*9800	3221	4156	3137	0871	8992	3978	1871	7281
.5	9210	7872	0650	9178	*9712	3133	4066	3045	0778	8898	3884	1776	7184
4	9117	7776	0554	9078	*9612	3032	3964	2940	0672	8792	3776	1667	7074
.5	9011	7667	0444	8964	*9498	2918	3848	2821	0553	8672	3654	1545	6950
					1.333								
5	8892	7546	0322	8838	9372	2791	3719	2690	0420	8538	3520	1410	6812
.5	8761	7412	0187	8699	9233	2651	3577	2545	0275	8392	3372	1262	6662
6	8617	7265	0040	8547	9081	2499	3422	2388	0117	8233	3212	1100	6499
.5	8461	7106	*9880	8383	8917	2334	3256	2219	*9947	8062	3039	0927	6324
7	8292	6935	*9708	8207	8740	2157	3077	2037	*9764	7878	2854	0741	6136
.5	8112	6752	*9525	8019	8552	1968	2886	1844	*9569	7683	2656	0543	5936
8	7920	6558	*9330	7819	8352	1767	2683	1638	*9363	7475	2447	0333	5724
.5	7717	6352	*9123	7607	8141	1555	2469	1420	*9144	7256	2226	0111	5500
9	7502	6134	*8904	7384	7918	1331	2243	1192	*8914	7025	1994	*9878	5264
.5	7276	5906	*8675	7150	7683	1096	2006	0951	*8673	6782	1750	*9633	5017
			1.331						1.337			1.340	
10	7040	5666	8434	6905	7438	0850	1757	0700	8420	6528	1494	9377	4758
.5	6792	5415	8183	6648	7181	0593	1498	0437	8157	6264	1228	9110	4489
11	6533	5154	7920	6381	6914	0325	1228	0164	7882	5988	0950	8831	4208
.5	6264	4882	7648	6104	6636	0046	0947	*9880	7597	5702	0662	8542	3916
12	5984	4599	7364	5815	6348	*9757	0655	*9585	7301	5404	0363	8242	3614
.5	5694	4306	7071	5517	6049	*9457	0353	*9279	6994	5097	0053	7932	3301
13	5394	4004	6767	5208	5740	*9147	0041	*8964	6677	4779	*9733	7611	2978
.5	5084	3690	6453	4889	5421	*8827	*9719	*8638	6350	4451	*9403	7280	2644
14	4764	3368	6129	4560	5092	*8498	*9386	*8302	6013	4112	*9063	6938	2300
.5	4435	3035	5795	4221	4753	*8158	*9044	*7956	5666	3764	*8713	6587	1946
						1.333	1.334	1.336			1.339		
15	4095	2692	5452	3872	4404	7808	8692	7601	5309	3406	8352	6226	1582
.5	3746	2340	5099	3514	4046	7449	8331	7236	4943	3038	7983	5855	1206
16	3388	1979	4737	3146	3678	7080	7960	6861	4567	2661	7603	5475	0825
.5	3020	1608	4365	2770	3301	6702	7579	6476	4181	2274	7214	5083	0432
17	2643	1228	3984	2383	2915	6315	7189	6083	3786	1878	6816	4685	0029
.5	2257	0839	3594	1988	2519	5919	6790	5680	3382	1472	6408	4276	*9618
18	1862	0441	3196	1584	2114	5513	6382	5268	2969	1057	5991	3858	*9196
.5	1459	0034	2788	1170	1701	5099	5965	4847	2546	0634	5565	3431	*8766
19	1046	*9619	2371	0748	1279	4676	5539	4417	2115	0201	5130	2995	*8327
.5	0625	*9194	1946	0317	0847	4244	5104	3979	1675	*9760	4686	2550	*7879
		1.330		1.332						1.337			1.342
20	0195	8761	1512	9877	0408	3803	4661	3531	1226	9309	4234	2096	7423
.5	*9757	8320	1069	9429	*9959	3354	4209	3075	0769	8850	3772	1634	6956
21	*9310	7870	0618	8973	*9503	2896	3749	2611	0303	8383	3302	1163	6482
.5	*8855	7412	0159	8508	*9038	2430	3280	2138	*9828	7907	2824	0684	5999
22	*8392	6945	*9692	8034	*8564	1956	2803	1656	*9346	7423	2338	0196	5508
.5	*7920	6471	*9216	7553	*8083	1473	2318	1167	*8854	6930	1842	*9699	5008
23	*7441	5988	*8733	7064	*7593	0983	1824	0669	*8355	6430	1339	*9195	4500
.5	*6954	5497	*8241	6566	*7095	0484	1323	0164	*7848	5921	0828	*8682	3983
24	*6458	4999	*7741	6061	*6590	*9978	0813	*9650	*7333	5404	0308	*8162	3459
.5	*5955	4492	*7234	5547	*6076	*9463	0296	*9128	*6809	4879	*9781	*7633	2926
	1.329		1.330		1.332	1.332	1.333	1.335	1.336		1.338	1.339	
25	5445	3978	6719	5026	5555	8941	9771	8599	6278	4347	9246	7096	2386
.5	4926	3456	6196	4497	5026	8411	9238	8061	5739	3806	8703	6552	1838
26	4400	2927	5666	3961	4490	7873	8697	7516	5193	3258	8152	6000	1282
.5	3866	2390	5128	3417	3945	7328	8149	6964	4639	2702	7593	5440	0718
27	3326	1846	4582	2866	3394	6776	7594	6404	4077	2139	7027	4872	0146
.5	2777	1294	4030	2307	2835	6216	7031	5836	3508	1568	6453	4297	*9567
28	2222	0735	3470	1740	2268	5648	6460	5261	2931	0990	5872	3715	*8980
.5	1659	0169	2902	1167	1695	5073	5882	4679	2347	0404	5284	3125	*8386
29	1089	*9595	2328	0586	1114	4492	5298	4089	1756	*9811	4688	2528	*7785
.5	0512	*9015	1746	*9998	0526	3902	4705	3492	1157	*9211	4085	1923	*7178
													1.343
	1.328	1.329		1.331	1.331					1.336			
30	9927	8427	1157	9403	9930	3308	4108	2888	0551	8603	3474	1311	6961

TABLE 5.—*Index of refraction of distilled water for various spectral lines*—Con.

[These values were computed by means of the general interpolation formula (see eq 3). Observations were made at the points indicated by bold-faced type; their deviations from these computed values are shown in figure 11. Read initial digits in same column above tabulated values unless asterisk refers to initial digits below]

t°C	Wave lengths in angstroms												
	7065.2	6678.1	6562.8	5892.6	5875.6	5769.6	5460.7	5015.7	4861.3	4713.1	4471.5	4358.3	4046.6
	1.328	1.329	1.330	1.331	1.331	1.332	1.333	1.335	1.336	1.336	1.338	1.339	1.341
30	**9927**	**8427**	**1157**	**9403**	**9930**	**3306**	**4106**	**2888**	**0551**	**8603**	**3474**	**1311**	**6561**
.5	9336	7832	0562	8801	9328	2703	3500	2277	*9939	7989	2857	0692	5937
31	8738	7231	*9959	8192	8719	2093	2886	1659	*9319	7367	2232	0066	5307
.5	8133	6622	*9350	7576	8103	1476	2266	1034	*8692	6739	1601	*9433	4669
32	7521	6007	*8733	6954	7480	0852	1639	0402	*8058	6103	0962	*8793	4025
.5	6903	5385	*8110	6324	6850	0221	1005	*9763	*7418	5461	0317	*8146	3373
33	6278	4756	*7480	5688	6214	*9583	0364	*9118	*6770	4812	*9664	*7492	2715
.5	5646	4121	*6844	5045	5571	*8939	*9717	*8466	*6116	4156	*9005	*6832	2050
34	5007	3479	*6200	4395	4921	*8288	*9063	*7806	*5455	3493	*8340	*6164	1378
.5	4362	2830	*5551	3739	4264	*7631	*8402	*7141	*4788	2824	*7667	*5490	0699
			1.329			1.331	1.332	1.334	1.335		1.337	1.338	
35	3711	2175	4894	3076	**3602**	6967	7735	**6469**	4114	2148	**6988**	4810	0014
.5	3053	1513	4232	2407	2932	6296	7061	5790	3433	1465	6302	4122	*9322
36	2388	0845	3563	1731	2256	5619	6381	5105	2746	0776	5610	3428	*8623
.5	1718	0171	2887	1049	1574	4936	5694	4413	2052	0081	4911	**2728**	*7918
37	1041	*9490	2205	0361	0886	4246	5001	3715	1352	*9379	4206	2021	*7206
.5	0357	*8803	1517	*9666	0191	3550	4302	3010	0646	*8671	3495	1308	*6488
38	*9668	*8110	0823	*8965	*9489	2848	3596	2300	*9934	*7956	2777	0588	*5763
.5	*8972	*7411	0122	*8258	*8782	2140	2885	1583	*9215	*7235	2052	*9863	*5032
39	*8270	*6705	*9416	*7544	*8069	1425	2167	0860	*8490	*6508	1322	*9130	*4295
.5	*7563	*5994	*8703	*6825	*7349	0704	1443	0130	*7758	*5775	0585	*8392	*3551
	1.327	1.328	1.328	1.330	1.330	1.330		1.333	1.334	1.335	1.336	1.337	1.340
40	**6849**	**5276**	**7984**	**6099**	**6623**	**9977**	**0712**	**9395**	**7021**	**5036**	**9842**	**7647**	**2801**
.5	6129	4552	7260	5368	5891	9244	*9976	8653	6277	4290	9094	6897	2045
41	5403	3823	6529	4630	5154	8506	*9234	7906	5528	3539	8338	6140	1283
.5	4671	3087	5792	3887	4410	7761	*8486	7152	4772	2781	7577	5377	0514
42	3934	2346	5050	3137	3660	7010	*7732	6393	4011	2018	6810	4608	*9740
.5	3190	1598	4301	2382	2905	6253	*6971	5627	3243	1248	6037	3833	*8960
43	2441	0845	3547	1621	2143	5491	*6205	4856	2470	0473	5258	3052	*8173
.5	1686	0086	2787	0854	1376	4722	*5434	4079	1691	*9691	4473	2266	*7381
44	0925	*9321	2021	0081	0603	3948	*4656	3296	0906	*8904	3682	1473	*6582
.5	0158	*8551	1249	*9302	*9825	3168	*3873	2507	0115	*8111	2886	0674	*5778
	1.326	1.327		1.329	1.329		1.331		1.333	1.334		1.336	1.339
45	9386	7775	0472	8518	9040	2383	3084	**1712**	9318	7313	**2083**	9870	4968
.5	8608	6993	*9689	7728	8250	1592	2289	0912	8516	6508	1275	9060	4152
46	7825	6206	*8900	6933	7454	0795	1489	0106	7708	5698	0461	**8244**	3330
.5	7036	5413	*8106	6132	6653	*9992	0683	*0295	6894	4882	*9642	7423	2503
47	6241	4614	*7307	5325	5846	*9184	*9871	*8478	6075	4061	*8816	6596	1670
.5	5441	3810	*6501	4512	5034	*8371	*9054	*7655	5250	3234	*7986	5763	0831
48	4636	3001	*5691	3695	4216	*7552	*8231	*6827	4420	2401	*7149	4924	*9986
.5	3824	2186	*4875	2872	3392	*6727	*7403	*5993	3584	1563	*6307	4080	*9136
49	3008	1366	*4053	2043	2564	*5897	*6570	*5154	2742	0720	*5459	3231	*8280
.5	2186	0540	*3226	1209	1729	*5061	*5730	*4309	1896	*9870	*4607	2376	*7419
		1.326	1.327			1.329	1.330	1.332		1.333	1.335		1.338
50	**1359**	**9709**	**2394**	**0369**	**0889**	**4221**	**4886**	**3459**	**1043**	**9016**	**3748**	**1515**	**6552**
.5	0527	8872	1556	*9524	0044	3374	4036	2603	0186	8156	2884	0649	5680
51	*9689	8030	0713	*8674	*9194	2523	3181	1742	*9322	7291	2015	*9778	4802
.5	*8846	7183	*9865	*7819	*8338	1666	2321	0876	*8454	6420	1140	*8901	3918
52	*7998	6331	*9011	*6958	*7477	0804	1455	0005	*7580	5544	0260	*8019	3030
.5	*7144	5473	*8152	*6092	*6611	*9936	0584	*9128	*6701	4663	*9375	*7131	2135
53	*6286	4610	*7288	*5221	*5740	*9064	*9708	*8246	*5817	3776	*8484	*6238	1236
.5	*5422	3742	*6419	*4344	*4863	*8186	*8826	*7358	*4927	2884	*7588	*5340	0331
54	*4553	2869	*5545	*3463	*3981	*7303	*7939	*6466	*4033	1987	*6687	*4437	*9421
.5	*3678	1991	*4665	*2576	*3094	*6415	*7048	*5568	*3133	1085	*5780	*3528	*8505
	1.325		1.326	1.328	1.328	1.328	1.329	1.331	1.332		1.334	1.335	1.337
55	**2799**	**1108**	**3781**	**1684**	**2202**	**5521**	**6151**	**4665**	**2227**	**0177**	**4863**	**2614**	**7584**
.5	1915	0219	2891	0787	1305	4623	5248	3757	1317	*9265	3952	1695	6658
56	1026	*9326	1996	*9885	0403	3720	4341	2844	0402	*8347	3030	0771	5727
.5	0131	*8427	1096	*8978	*9496	2811	3429	1926	*9482	*7424	2102	*9842	4791
57	*9232	*7524	0192	*8066	*8583	1898	2512	1003	*8556	*6496	1170	*8907	3849
.5	*8328	*6615	*9282	*7148	*7666	0979	1590	0075	*7625	*5563	0233	*7968	2902
58	*7418	*5702	*8367	*6226	*6743	0055	0662	*9141	*6690	*4625	*9290	*7023	1950
.5	*6504	*4783	*7447	*5299	*5816	*9127	*9730	*8203	*5749	*3682	*8343	*6073	0994
59	*5585	*3860	*6523	*4367	*4884	*8193	*8793	*7260	*4803	*2734	*7390	*5118	0031
.5	*4661	*2931	*5593	*3430	*3947	*7255	*7850	*6312	*3853	*1781	*6433	*4159	*9064
	1.324	1.325	1.325	1.327	1.327	1.327	1.328	1.330	1.331	1.332	1.333	1.334	1.336
60	**3732**	**1998**	**4659**	**2483**	**3005**	**6312**	**6904**	**5358**	**2897**	**0823**	**5471**	**3194**	**8092**

TABLE 6.—*Sodium-lines index of refraction of distilled water*

t°C	Tenths of degrees										Mean differences	n_{5378} minus n_{5893} (a)
	0	1	2	3	4	5	6	7	8	9		
0	1.333 9493	9494	9494	9494	9493	9491	9489	9486	9483	9479	2	535
1	9474	9469	9464	9458	9451	9443	9435	9427	9418	9408	7	535
2	9398	9387	9376	9364	9351	9338	9325	9310	9296	9281	13	535
3	9265	9249	9232	9214	9196	9178	9159	9139	9119	9099	18	534
4	9078	9056	9034	9011	8988	8964	8940	8915	8890	8864	24	534
5	8838	8811	8784	8756	8727	8699	8669	8639	8609	8578	29	534
6	8547	8515	8483	8450	8417	8383	8349	8314	8279	8243	34	534
7	8207	8170	8133	8095	8057	8019	7980	7940	7900	7860	38	534
8	7819	7777	7736	7693	7650	7607	7564	7519	7475	7430	43	533
9	7384	7338	7292	7245	7198	7150	7102	7053	7004	6955	48	533
10	6905	6854	6804	6752	6700	6648	6596	6543	6489	6436	52	533
11	6381	6327	6271	6216	6160	6104	6047	5989	5932	5874	56	533
12	5815	5756	5697	5637	5577	5517	5456	5394	5332	5270	60	532
13	5208	5145	5081	5018	4953	4889	4824	4758	4692	4626	64	532
14	4560	4493	4425	4358	4289	4221	4152	4083	4013	3943	68	532
15	3872	3802	3730	3659	3587	3514	3441	3368	3295	3221	72	532
16	3146	3072	2997	2921	2846	2770	2693	2616	2539	2461	76	531
17	2383	2305	2226	2147	2068	1988	1908	1827	1746	1665	80	531
18	1584	1502	1419	1336	1254	1170	1086	1002	0918	0833	83	531
19	0748	0662	0576	0490	0404	0317	0230	0142	0054	*9966	87	531
20	1.332 9877	9788	9699	9609	9520	9429	9339	9248	9156	9065	90	530
21	8973	8880	8788	8695	8601	8508	8414	8319	8225	8130	94	530
22	8034	7939	7843	7746	7650	7553	7456	7358	7260	7162	97	530
23	7064	6965	6866	6766	6666	6566	6466	6365	6264	6162	100	529
24	6061	5959	5856	5754	5651	5547	5444	5340	5236	5131	103	529
25	5026	4921	4816	4710	4604	4497	4391	4284	4176	4069	106	529
26	3961	3853	3744	3635	3526	3417	3307	3197	3087	2976	109	528
27	2866	2754	2643	2531	2419	2307	2194	2081	1968	1854	112	528
28	1740	1626	1512	1397	1282	1167	1051	0935	0819	0703	115	528
29	0586	0469	0352	0234	0116	*9998	*9880	*9761	*9642	*9523	118	527
30	1.331 9403	9283	9163	9043	8922	8801	8680	8558	8437	8315	121	527
31	8192	8070	7947	7824	7700	7576	7452	7328	7203	7079	124	527
32	6954	6828	6702	6577	6450	6324	6197	6070	5943	5815	126	526
33	5688	5560	5431	5303	5174	5045	4915	4786	4656	4525	129	526
34	4395	4264	4133	4002	3871	3739	3607	3474	3342	3209	132	526
35	3076	2943	2809	2675	2541	2407	2272	2137	2002	1867	134	525
36	1731	1595	1459	1323	1186	1049	0912	0774	0637	0499	137	525
37	0361	0222	0083	*9944	*9805	*9666	*9526	*9386	*9246	*9106	139	525
38	1.330 8965	8824	8683	8541	8400	8258	8116	7973	7830	7688	142	524
39	7544	7401	7257	7113	6969	6825	6680	6535	6390	6245	144	524
40	6099	5954	5807	5661	5514	5368	5221	5073	4926	4778	147	524
41	4630	4482	4333	4185	4036	3887	3737	3588	3438	3288	149	523
42	3137	2986	2836	2685	2533	2382	2230	2078	1926	1773	152	523
43	1621	1468	1314	1161	1008	0854	0699	0545	0391	0236	154	523
44	0081	*9926	*9770	*9614	*9458	*9302	*9146	*8989	*8832	*8675	156	522
45	1.329 8518	8361	8203	8045	7886	7728	7569	7411	7252	7092	158	522
46	6933	6773	6613	6453	6292	6132	5971	5810	5648	5487	160	521
47	5325	5163	5001	4838	4675	4512	4349	4186	4022	3859	163	521
48	3695	3531	3366	3202	3037	2872	2706	2541	2375	2209	165	521
49	2043	1876	1710	1543	1376	1209	1041	0874	0706	0538	167	520
50	0369	0201	0032	*9863	*9694	*9524	*9355	*9185	*9015	*8845	169	520
51	1.328 8674	8504	8333	8162	7990	7819	7647	7475	7303	7131	171	520
52	6958	6785	6612	6439	6266	6092	5918	5744	5570	5396	174	519
53	5221	5046	4871	4696	4520	4344	4168	3992	3816	3639	176	519
54	3463	3286	3109	2931	2754	2576	2398	2220	2041	1863	178	518
55	1684	1505	1326	1146	0967	0787	0607	0427	0246	0066	180	518
56	1.327 9885	9704	9523	9341	9160	8978	8796	8614	8431	8248	182	518
57	8066	7883	7699	7516	7332	7148	6964	6780	6596	6411	184	517
58	6226	6041	5856	5671	5485	5299	5113	4927	4741	4554	186	517
59	4367	4180	3993	3806	3618	3430	3242	3054	2866	2677	188	516
60	2488											

* To get n_{5378} add $10^{-7}\times(n_{5378}-n_{5893})$ as tabulated in right-hand column.

TABLE 7.—*General interpolation table for index of refraction of distilled water*

t°C	Wave lengths in angstroms										$-10^7\times\frac{dn}{d\lambda}$ (λ=4200Å)
	4000 (extrapolated)	4020 (extrapolated)	4040 (extrapolated)	4060	4080	4100	4120	4140	4160	4180	
0	1.34 41907	40022	38166	36340	34542	32771	31028	29312	27621	25956	3.6
1	41871	39986	38131	36304	34506	32736	30993	29277	27586	25922	63.9
2	41776	39891	38036	36210	34412	32642	30899	29183	27493	25828	122.1
3	41623	39739	37884	36058	34260	32490	30748	29032	27342	25678	178.4
4	41415	39531	37676	35850	34053	32284	30541	28826	27136	25472	232.8
5	41154	39269	37415	35589	33792	32023	30281	28566	26876	25212	285.5
6	40840	38956	37102	35276	33480	31711	29969	28254	26564	24900	336.6
7	40476	38592	36738	34913	33117	31348	29606	27891	26202	24539	386.0
8	40063	38179	36326	34501	32705	30936	29195	27480	25792	24128	434.1
9	39602	37719	35866	34042	32246	30478	28736	27022	25334	23671	480.7
$-10^7\times\frac{dn_{10}}{d\lambda}$	=94.92	93.40	91.93	90.49	89.08	87.71	86.37	85.06	83.77	82.52	
10	1.34 39096	37213	35360	33536	31740	29973	28232	26518	24830	23167	526.0
11	38545	36662	34810	32986	31190	29423	27682	25969	24281	22618	570.0
12	37950	36068	34215	32392	30597	28830	27090	25376	23689	22027	612.8
13	37313	35431	33579	31756	29961	28194	26454	24742	23054	21392	654.6
14	36634	34753	32901	31078	29284	27518	25778	24065	22379	20717	695.3
15	35916	34035	32183	30361	28567	26801	25062	23349	21663	20002	734.9
16	35158	33277	31426	29604	27810	26044	24306	22594	20908	19247	773.6
17	34361	32481	30630	28809	27016	25250	23512	21800	20114	18454	811.4
18	33528	31648	29797	27976	26183	24418	22680	20969	19284	17624	848.2
19	32657	30778	28928	27107	25314	23550	21812	20102	18417	16757	884.2
20	31751	29872	28022	26202	24410	22646	20909	19198	17514	15855	919.4
21	30810	28931	27082	25262	23471	21707	19970	18260	16576	14918	953.9
22	29835	27956	26108	24288	22497	20734	18998	17288	15605	13946	987.7
23	28826	26948	25100	23281	21490	19728	17992	16283	14600	12942	1020.7
24	27784	25907	24059	22241	20450	18688	16953	15244	13562	11904	1053.1
25	26710	24833	22986	21168	19379	17617	15882	14174	12492	10835	1084.9
26	25605	23728	21882	20064	18275	16514	14780	13072	11390	09734	1116.0
27	24468	22592	20746	18930	17141	15380	13646	11939	10258	08602	1146.5
28	23301	21426	19581	17764	15976	14216	12483	10776	09096	07440	1176.5
29	22104	20230	18385	16569	14782	13022	11289	09583	07903	06248	1206.0
$-10^7\times\frac{dn_{20}}{d\lambda}$	=94.48	92.96	91.49	90.06	88.65	87.28	85.93	84.62	83.35	82.10	
30	1.34 20878	19004	17160	15345	13558	11798	10066	08361	06682	05027	1235.0
31	19623	17750	15906	14092	12305	10546	08815	07110	05431	03777	1263.4
32	18340	16467	14624	12810	11024	09266	07535	05831	04153	02499	1291.4
33	17030	15157	13314	11501	09716	07958	06228	04524	02846	01194	1319.0
34	15690	13818	11976	10164	08379	06622	04893	03190	01512	*99860	1346.1
35	14324	12453	10612	08800	07016	05260	03531	01828	00152	*98500	1372.8
36	12932	11061	09221	07409	05626	03871	02142	00440	*98764	*97114	1399.1
37	11513	09643	07804	05993	04210	02455	00728	*99027	*97351	*95701	1425.0
38	10068	08199	06360	04550	02768	01014	*99287	*97586	*95912	*94263	1450.5
39	08598	06730	04892	03082	01301	*99548	*97822	*96122	*94448	*92799	1475.7
40	07103	05236	03398	01589	*99809	*98056	*96331	*94632	*92958	*91310	1500.6
41	05583	03716	01879	00071	*98292	*96540	*94815	*93117	*91444	*89796	1525.1
42	04038	02172	00336	*98529	*96750	*94999	*93275	*91577	*89905	*88259	1549.3
43	02470	00604	*98769	*96963	*95184	*93434	*91711	*90014	*88343	*86697	1573.2
44	00877	*99013	*97178	*95372	*93595	*91845	*90123	*88426	*86756	*85111	1596.8
45	1.33 99260	97397	95563	93758	91982	90233	88511	86816	85146	83502	1620.0
46	97621	95758	93926	92121	90346	88598	86877	85182	83513	81869	1643.1
47	95958	94097	92264	90461	88686	86939	85219	83525	81857	80214	1665.8
48	94273	92412	90581	88778	87004	85258	83539	81846	80178	78536	1688.4
49	92565	90705	88874	87073	85300	83554	81836	80144	78477	76836	1710.7
$-10^7\times\frac{dn_{30}}{d\lambda}$	=93.72	92.21	90.74	89.32	87.92	86.56	85.22	83.92	82.65	81.40	
50	1.33 90834	88975	87146	85345	83573	81828	80111	78419	76754	75113	1732.7
51	89082	87224	85395	83596	81824	80080	78364	76673	75009	73369	1754.5
52	87308	85451	83623	81824	80054	78311	76595	74905	73241	71603	1776.2
53	85512	83656	81829	80031	78262	76520	74805	73116	71453	69815	1797.4
54	83694	81839	80014	78217	76448	74707	72993	71305	69643	68006	1818.7
55	81856	80002	78177	76381	74614	72873	71160	69474	67812	66176	1839.6
56	79996	78143	76320	74525	72758	71019	69307	67621	65960	64325	1860.4
57	78116	76264	74441	72647	70882	69143	67432	65747	64088	62454	1880.9
58	76214	74364	72542	70749	68985	67248	65537	63853	62195	60562	1901.3
59	74293	72443	70623	68831	67067	65331	63622	61939	60282	58649	1921.6
60	72351	70502	68683	66892	65130	63395	61686	60004	58348	56716	1941.8

TABLE 7.—*General interpolation table for index of refraction of distilled water*—Con.

t°C	Wave lengths in angstroms										
	4200	4220	4240	4260	4280	4300	4320	4340	4360	4380	4400
0	1.34 24315	22699	21107	19538	17991	16467	14965	13484	12024	10584	09164
1	24281	22666	21073	19504	17958	16434	14932	13451	11991	10552	09132
2	24188	22572	20980	19412	17866	16342	14840	13360	11900	10460	09041
3	24038	22422	20830	19262	17716	16193	14691	13211	11752	10312	08893
4	23832	22217	20625	19057	17511	15988	14486	13006	11547	10108	08689
5	23573	21958	20366	18798	17253	15730	14229	12749	11290	09851	08432
6	23261	21647	20056	18488	16943	15420	13919	12439	10980	09542	08124
7	22900	21286	19695	18127	16582	15060	13559	12080	10621	09183	07765
8	22490	20876	19285	17718	16173	14651	13150	11671	10213	08775	07357
9	22032	20418	18828	17261	15717	14195	12695	11216	09758	08320	06902
$-10^7\times\frac{dn_{10}}{d\lambda}$	81.29	80.08	78.92	77.77	76.64	75.54	74.46	73.41	72.38	71.37	70.38
10	1.34 21529	19915	18326	16759	15215	13693	12193	10714	09257	07819	06402
11	20981	19368	17778	16212	14668	13146	11647	10168	08711	07274	05857
12	20389	18776	17187	15621	14078	12556	11057	09579	08122	06685	05269
13	19756	18143	16554	14988	13445	11924	10425	08948	07491	06054	04638
14	19080	17468	15879	14314	12771	11251	09752	08275	06818	05382	03966
15	18365	16753	15165	13600	12058	10538	09039	07562	06106	04670	03255
16	17611	15999	14412	12847	11305	09785	08287	06810	05355	03919	02504
17	16818	15207	13620	12055	10514	08994	07497	06021	04565	03130	01715
18	15989	14378	12791	11227	09685	08166	06669	05194	03738	02304	00889
19	15122	13512	11925	10362	08821	07302	05805	04330	02875	01441	00027
20	14220	12610	11024	09461	07920	06402	04906	03431	01977	00543	*99129
21	13284	11674	10088	08526	06986	05468	03972	02497	01043	*99610	*98197
22	12313	10704	09118	07556	06016	04499	03004	01529	00076	*98643	*97230
23	11309	09700	08115	06553	05014	03497	02002	00528	*99075	*97643	*96230
24	10272	08664	07079	05518	03979	02462	00968	*99495	*98042	*96610	*95198
25	09203	07595	06011	04450	02912	01396	*99902	*98429	*96977	*95545	*94134
26	08102	06495	04912	03351	01813	00298	*98804	*97332	*95880	*94449	*93038
27	06971	05364	03781	02221	00684	*99169	*97676	*96204	*94753	*93322	*91911
28	05810	04203	02621	01061	*99524	*98010	*96517	*95046	*93595	*92165	*90755
29	04618	03012	01430	*99872	*98335	*96821	*95329	*93858	*92408	*90978	*89569
$-10^7\times\frac{dn_{20}}{d\lambda}$	80.86	79.66	78.50	77.36	76.23	75.13	74.04	73.00	71.97	70.96	69.98
30	1.34 03398	01793	00211	*98653	*97117	*95604	*94112	*92642	*91192	*89763	*88354
31	02148	00544	*98963	*97405	*95870	*94357	*92866	*91396	*89947	*88518	*87110
32	00871	*99267	*97687	*96129	*94595	*93082	*91592	*90123	*88674	*87246	*85838
33	1.33 99566	97962	96383	94826	93292	91780	90290	88821	87373	85946	84538
34	98233	96630	95051	93495	91962	90450	88961	87493	86045	84618	83211
35	96874	95272	93693	92137	90604	89094	87605	86138	84690	83264	81858
36	95488	93886	92308	90753	89221	87711	86223	84756	83310	81884	80478
37	94076	92475	90897	89343	87811	86302	84814	83348	81902	80477	79072
38	92638	91038	89461	87907	86376	84867	83380	81915	80470	79045	77640
39	91175	89575	87999	86446	84916	83408	81921	80456	79012	77587	76183
40	89687	88088	86512	84960	83430	81923	80437	78972	77529	76105	74702
41	88174	86576	85001	83449	81920	80413	78928	77464	76021	74598	73195
42	86637	85039	83465	81914	80386	78880	77395	75932	74489	73067	71665
43	85076	83479	81905	80355	78827	77322	75838	74376	72934	71512	70110
44	83490	81894	80322	78772	77243	75740	74257	72796	71354	69933	68532
45	81882	80287	78715	77166	75640	74136	72653	71192	69752	68331	66931
46	80250	78656	77085	75536	74011	72508	71026	69566	68126	66706	65307
47	78596	77002	75432	73884	72359	70857	69376	67916	66477	65058	63659
48	76919	75326	73756	72209	70685	69184	67703	66244	64806	63388	61990
49	75219	73627	72058	70512	68989	67488	66008	64550	63112	61695	60298
$-10^7\times\frac{dn_{30}}{d\lambda}$	80.18	78.98	77.83	76.70	75.57	74.48	73.40	72.36	71.34	70.33	69.35
50	1.33 73498	71906	70338	68793	67270	65770	64291	62834	61397	59980	58584
51	71754	70163	68596	67052	65530	64030	62552	61096	59660	58244	56848
52	69989	68399	66832	65289	63768	62269	60792	59336	57901	56486	55090
53	68202	66613	65047	63504	61984	60486	59010	57555	56120	54706	53312
54	66394	64806	63241	61699	60180	58683	57207	55753	54319	52905	51512
55	64565	62977	61413	59872	58354	56858	55383	53929	52496	51084	49691
56	62715	61128	59565	58025	56508	55012	53538	52085	50653	49241	47849
57	60844	59258	57696	56157	54640	53146	51673	50221	48789	47378	45987
58	58953	57368	55807	54269	52753	51259	49787	48336	46905	45495	44104
59	57041	55458	53897	52360	50845	49352	47881	46431	45001	43591	42202
60	55110	53527	51968	50431	48917	47425	45955	44505	43076	41668	40279

TABLE 7.—*General interpolation table for index of refraction of distilled water*—Con.

t°C	Wave lengths in angstroms										$-10^7\times\frac{dn}{d\lambda}$ (λ=4600A)
	4400	4420	4440	4460	4480	4500	4520	4540	4560	4580	
0	1.34 09164	07764	06383	05021	03678	02352	01044	*99753	*98480	*97223	0.0
1	09132	07732	06352	04990	03646	02321	01013	*99722	*98449	*97192	60.1
2	09041	07641	06261	04899	03556	02230	00923	*99633	*98359	*97102	118.1
3	08893	07492	06112	04750	03408	02083	00776	*99486	*98213	*96956	174.1
4	08689	07290	05910	04549	03206	01881	00574	*99284	*98011	*96754	228.4
5	08432	07033	05653	04292	02950	01625	00318	*99028	*97756	*96500	280.8
6	08124	06725	05345	03984	02642	01318	00011	*98721	*97449	*96193	331.6
7	07765	06366	04987	03626	02284	00960	*99653	*98364	*97092	*95836	380.9
8	07357	05959	04580	03220	01878	00554	*99247	*97959	*96687	*95431	428.6
9	06902	05504	04126	02766	01424	00100	*98794	*97506	*96234	*94979	474.0
$-10^7\times\frac{dn_{10}}{d\lambda}$	−70.38	69.40	68.45	67.53	66.62	65.72	64.85	63.99	63.16	62.33	
10	1.34 06402	05004	03626	02266	00925	*99601	*98296	*97007	*95736	*94481	520.1
11	05857	04460	03081	01722	00381	*99058	*97752	*96464	*95193	*93939	562.9
12	05269	03871	02494	01134	*99794	*98471	*97166	*95878	*94607	*93353	603.5
13	04638	03241	01864	00505	*99164	*97842	*96537	*95250	*93979	*92726	642.0
14	03966	02570	01193	*99834	*98494	*97172	*95868	*94580	*93310	*92057	678.5
15	03255	01858	00482	*99124	*97784	*96462	*95158	*93871	*92602	*91348	727.9
16	02504	01108	*99732	*98374	*97034	*95713	*94409	*93123	*91854	*90601	766.4
17	01715	00320	*98944	*97586	*96247	*94926	*93623	*92337	*91068	*89815	803.8
18	00889	*99494	*98118	*96761	*95423	*94102	*92799	*91513	*90245	*88993	840.5
19	00027	*98632	*97257	*95900	*94562	*93242	*91939	*90654	*89386	*88134	876.3
20	1.33 99129	97735	96360	95004	93666	92346	91044	89759	88491	87239	911.3
21	98197	96803	95428	94072	92735	91415	90113	88829	87562	86310	945.6
22	97230	95837	94462	93107	91770	90451	89150	87866	86598	85348	979.1
23	96230	94837	93464	92109	90772	89453	88152	86869	85602	84352	1011.9
24	95198	93805	92432	91078	89741	88423	87122	85839	84573	83323	1044.1
25	94134	92741	91369	90014	88679	87361	86061	84778	83512	82263	1075.6
26	93038	91646	90274	88920	87585	86268	84968	83686	82420	81171	1106.6
27	91911	90520	89148	87795	86460	85144	83844	82562	81298	80049	1136.9
28	90755	89364	87993	86640	85306	83989	82690	81409	80145	78897	1166.6
29	89569	88179	86808	85456	84122	82806	81507	80226	78963	77715	1195.9
$-10^7\times\frac{dn_{20}}{d\lambda}$	−69.98	69.00	68.05	67.13	66.22	65.33	64.45	63.60	62.76	61.94	
30	1.33 88354	86964	85593	84242	82908	81593	80295	79015	77751	76504	1224.6
31	87110	85720	84351	82999	81666	80352	79054	77774	76512	75265	1252.9
32	85838	84449	83080	81729	80397	79082	77786	76506	75244	73998	1280.7
33	84538	83150	81781	80431	79099	77785	76489	75210	73948	72703	1308.0
34	83211	81824	80456	79106	77774	76461	75166	73887	72626	71381	1334.9
35	81858	80471	79103	77754	76423	75110	73815	72538	71277	70032	1361.4
36	80478	79091	77724	76376	75045	73733	72439	71161	69901	68657	1387.5
37	79072	77686	76319	74971	73642	72330	71036	69759	68500	67256	1413.1
38	77640	76255	74889	73542	72213	70902	69608	68332	67073	65830	1438.5
39	76183	74799	73433	72087	70758	69448	68155	66879	65621	64378	1463.5
40	74702	73318	71953	70607	69279	67969	66677	65402	64144	62902	1488.1
41	73195	71812	70448	69102	67775	66466	65174	63900	62642	61401	1512.4
42	71665	70282	68919	67574	66247	64938	63647	62374	61117	59876	1536.4
43	70110	68728	67366	66021	64695	63387	62097	60824	59567	58327	1560.1
44	68532	67151	65789	64445	63120	61812	60522	59250	57994	56755	1583.5
45	66931	65550	64189	62846	61521	60214	58925	57653	56398	55159	1606.5
46	65307	63927	62566	61223	59899	58593	57305	56033	54779	53541	1629.3
47	63659	62280	60920	59578	58255	56949	55661	54391	53137	51900	1652.0
48	61990	60611	59252	57911	56588	55283	53996	52726	51473	50236	1674.2
49	60298	58920	57561	56221	54898	53594	52308	51039	49786	48550	1696.2
$-10^7\times\frac{dn_{30}}{d\lambda}$	−69.35	68.38	67.44	66.52	65.62	64.74	63.86	63.01	62.18	61.37	
50	1.33 58584	57206	55848	54509	53187	51884	50598	49330	48078	46842	1718.1
51	56848	55471	54114	52775	51454	50152	48866	47599	46347	45113	1739.7
52	55090	53714	52358	51020	49700	48398	47113	45846	44596	43362	1761.0
53	53312	51936	50580	49243	47924	46623	45339	44072	42823	41589	1782.2
54	51512	50137	48782	47446	46127	44826	43543	42278	41028	39796	1803.2
55	49691	48317	46963	45627	44309	43009	41727	40462	39214	37982	1823.9
56	47849	46476	45123	43788	42471	41171	39890	38626	37378	36146	1844.5
57	45987	44615	43262	41928	40612	39313	38032	36769	35522	34291	1864.8
58	44104	42733	41381	40048	38732	37434	36154	34892	33645	32416	1885.0
59	42202	40831	39480	38147	36833	35536	34256	32994	31749	30520	1905.1
60	40279	38909	37559	36227	34913	33617	32338	31077	29832	28604	1924.8

TABLE 7.—*General interpolation table for index of refraction of distilled water*—Con.

t°C	Wave lengths in angstroms										
	4600	4620	4640	4660	4680	4700	4720	4740	4760	4780	4800
0	1.33 95982	94757	93548	92357	91175	90011	88862	87726	86605	85498	84403
1	95951	94727	93518	92324	91146	89982	88832	87698	86577	85469	84375
2	95862	94638	93429	92235	91057	89894	88744	87610	86489	85381	84288
3	95716	94492	93283	92090	90912	89748	88599	87465	86344	85237	84143
4	95514	94290	93082	91889	90711	89548	88399	87265	86144	85038	83944
5	95260	94036	92828	91635	90457	89294	88146	87012	85891	84785	83692
6	94954	93730	92522	91330	90152	88989	87841	86707	85587	84481	83388
7	94597	93374	92166	90974	89797	88634	87486	86353	85233	84127	83034
8	94192	92969	91762	90570	89393	88231	87083	85950	84830	83724	82632
9	93740	92518	91310	90119	88942	87780	86633	85500	84380	83275	82182
$-10^7\times\frac{dn_{10}}{d\lambda}$	−61.52	60.73	59.96	59.20	58.45	57.72	57.00	56.30	55.61	54.93	54.27
10	1.33 93243	92020	90813	89622	88446	87284	86137	85004	83885	82780	81688
11	92701	91478	90272	89081	87905	86743	85596	84464	83345	82240	81148
12	92115	90894	89687	88496	87320	86160	85013	83881	82762	81658	80566
13	91488	90266	89061	87870	86694	85534	84387	83256	82137	81033	79942
14	90820	89598	88393	87203	86027	84867	83721	82589	81472	80368	79277
15	90111	88890	87685	86495	85320	84160	83015	81884	80766	79662	78572
16	89364	88144	86939	85749	84575	83415	82270	81139	80022	78918	77828
17	88579	87359	86154	84965	83791	82632	81487	80356	79239	78136	77046
18	87757	86537	85333	84144	82970	81811	80667	79536	78420	77317	76228
19	86898	85679	84475	83287	82113	80955	79810	78681	77564	76462	75373
20	86004	84785	83582	82394	81221	80063	78919	77789	76674	75572	74483
21	85076	83857	82654	81467	80294	79136	77993	76864	75748	74647	73558
22	84114	82895	81693	80505	79333	78176	77033	75904	74789	73688	72600
23	83118	81900	80698	79511	78339	77182	76040	74911	73797	72696	71609
24	82090	80872	79671	78484	77313	76156	75014	73886	72772	71672	70585
25	81030	79813	78612	77426	76255	75098	73957	72829	71716	70616	69529
26	79939	78722	77522	76336	75165	74010	72868	71741	70628	69528	68442
27	78817	77601	76401	75216	74045	72890	71749	70622	69510	68411	67325
28	77665	76450	75250	74065	72896	71741	70600	69474	68362	67263	66178
29	76484	75269	74069	72885	71716	70562	69422	68296	67184	66086	65001
$-10^7\times\frac{dn_{20}}{d\lambda}$	−61.13	60.34	59.57	58.81	58.06	57.34	56.62	55.92	55.23	54.55	53.89
30	1.33 75274	74059	72860	71676	70507	69354	68214	67089	65978	64880	63796
31	74035	72821	71622	70439	69271	68117	66978	65854	64743	63645	62562
32	72768	71554	70356	69174	68006	66853	65714	64590	63480	62383	61300
33	71474	70261	69063	67881	66714	65561	64423	63299	62190	61093	60010
34	70152	68940	67743	66561	65394	64242	63105	61981	60872	59776	58694
35	68804	67592	66395	65214	64048	62897	61760	60637	59528	58433	57351
36	67430	66218	65022	63841	62676	61525	60388	59266	58158	57063	55981
37	66029	64818	63623	62443	61278	60127	58991	57869	56762	55667	54586
38	64604	63393	62198	61018	59854	58704	57568	56447	55340	54246	53166
39	63152	61943	60748	59569	58405	57256	56121	55000	53893	52800	51720
40	61677	60467	59274	58095	56932	55783	54648	53528	52422	51329	50250
41	60176	58968	57774	56596	55434	54285	53152	52032	50926	49834	48755
42	58652	57444	56251	55074	53912	52764	51630	50512	49406	48315	47236
43	57104	55896	54704	53528	52366	51218	50086	48967	47863	46772	45694
44	55532	54325	53134	51957	50796	49650	48518	47400	46296	45205	44128
45	53937	52731	51540	50364	49204	48058	46926	45809	44705	43615	42539
46	52319	51114	49923	48748	47588	46443	45312	44195	43092	42003	40927
47	50678	49473	48284	47109	45950	44805	43675	42559	41456	40368	39292
48	49015	47811	46622	45448	44289	43145	42016	40900	39798	38710	37635
49	47330	46126	44938	43765	42607	41463	40334	39219	38118	37030	35956
$-10^7\times\frac{dn_{30}}{d\lambda}$	−60.56	59.77	59.01	58.25	57.51	56.78	56.07	55.37	54.69	54.02	53.36
50	1.33 45623	44420	43232	42060	40902	39759	38631	37516	36416	35329	34255
51	43894	42692	41505	40333	39176	38033	36906	35792	34692	33605	32532
52	42144	40942	39755	38584	37428	36286	35159	34046	32947	31861	30788
53	40372	39171	37985	36815	35659	34518	33391	32279	31180	30095	29023
54	38579	37379	36194	35024	33869	32728	31603	30491	29393	28308	27237
55	36766	35566	34382	33212	32058	30918	29793	28682	27584	26500	25430
56	34932	33732	32549	31380	30226	29088	27963	26852	25756	24672	23602
57	33077	31878	30695	29528	28375	27236	26112	25003	23906	22824	21754
58	31202	30004	28822	27655	26502	25365	24242	23132	22037	20955	19886
59	29307	28110	26928	25762	24610	23473	22351	21242	20147	19066	17998
60	27392	26196	25015	23849	22698	21562	20440	19332	18238	17157	16090

TABLE 7.—*General interpolation table for index of refraction of distilled water*—Con.

t°C	Wave lengths in angstroms										$-10^7\times\frac{dn}{d\lambda}$ (λ = 5000 A)
	4800	4820	4840	4860	4880	4900	4920	4940	4960	4980	
0	1.33 84403	83322	82254	81199	80156	79125	78106	77099	76103	75119	[−2.4]
1	84375	83294	82226	81171	80128	79097	78078	77072	76076	75092	88.4
2	84288	83207	82139	81084	80041	79011	77992	76985	75990	75006	114.2
3	84143	83063	81995	80940	79898	78868	77849	76842	75848	74864	170.0
4	83944	82864	81796	80742	79699	78669	77651	76645	75650	74667	222.9
5	83692	82612	81544	80490	79448	78418	77400	76394	75399	74416	276.1
6	83388	82308	81241	80187	79145	78115	77098	76092	75097	74114	326.8
7	83034	81954	80888	79834	78792	77763	76745	75740	74746	73763	373.7
8	82632	81552	80486	79432	78391	77362	76345	75339	74345	73363	422.3
9	82182	81103	80037	78984	77943	76914	75897	74892	73898	72916	469.5
$-10^7\times\frac{dn_{10}}{d\lambda}$	−54.27	53.62	52.98	52.35	51.73	51.13	50.53	49.95	49.38	48.82	
10	1.33 81688	80609	79543	78490	77449	76420	75404	74399	73406	72424	514.4
11	81148	80070	79004	77951	76911	75883	74866	73862	72869	71887	557.9
12	80566	79488	78423	77370	76330	75302	74286	73282	72289	71308	600.4
13	79942	78864	77799	76747	75707	74679	73664	72660	71667	70686	641.7
14	79277	78199	77135	76083	75043	74016	73000	71997	71005	70024	681.9
15	78572	77495	76430	75379	74340	73313	72298	71294	70302	69322	721.2
16	77828	76751	75687	74636	73597	72570	71556	70553	69561	68581	759.4
17	77046	75970	74906	73855	72817	71791	70776	69774	68783	67803	796.7
18	76228	75152	74088	73038	72000	70974	69960	68958	67967	66988	833.3
19	75373	74297	73235	72184	71146	70121	69107	68106	67115	66136	868.8
20	74483	73408	72345	71295	70258	69233	68220	67218	66228	65249	903.7
21	73558	72484	71421	70372	69335	68310	67297	66296	65306	64328	937.8
22	72600	71526	70464	69415	68378	67354	66341	65340	64351	63373	971.1
23	71609	70534	69473	68424	67388	66364	65352	64352	63363	62385	1003.8
24	70585	69511	68450	67402	66366	65342	64331	63331	62342	61365	1035.8
25	69529	68456	67395	66348	65312	64289	63278	62278	61290	60313	1067.2
26	68442	67370	66309	65262	64227	63204	62193	61194	60207	59230	1097.9
27	67325	66253	65193	64146	63111	62089	61079	60080	59093	58117	1128.0
28	66178	65106	64046	63000	61966	60944	59934	58936	57949	56972	1157.7
29	65001	63930	62871	61825	60791	59769	58760	57762	56776	55801	1186.9
$-10^7\times\frac{dn_{20}}{d\lambda}$	−53.89	53.24	52.60	51.98	51.36	50.75	50.16	49.58	49.01	48.45	
30	1.33 63796	62724	61666	60620	59587	58566	57557	56560	55574	54599	1215.4
31	62552	61491	60433	59388	58355	57334	56326	55329	54343	53369	1243.5
32	61300	60229	59172	58127	57095	56075	55066	54070	53085	52112	1271.1
33	60010	58940	57884	56839	55807	54788	53780	52784	51800	50826	1298.3
34	58694	57624	56568	55524	54493	53474	52466	51471	50487	49514	1325.1
35	57351	56282	55226	54183	53152	52133	51126	50131	49148	48175	1351.4
36	55981	54913	53858	52815	51785	50766	49760	48765	47782	46810	1377.3
37	54586	53518	52464	51421	50391	49374	48368	47374	46391	45420	1402.9
38	53166	52098	51044	50002	48973	47956	46950	45957	44975	44004	1428.1
39	51720	50653	49600	48558	47529	46513	45508	44515	43533	42563	1452.9
40	50250	49184	48130	47089	46061	45045	44041	43048	42067	41097	1477.4
41	48755	47690	46637	45596	44569	43553	42549	41557	40576	39607	1501.6
42	47236	46171	45119	44079	43052	42037	41034	40042	39062	38093	1525.4
43	45694	44629	43578	42538	41512	40497	39494	38503	37524	36556	1548.9
44	44128	43064	42013	40974	39948	38934	37932	36941	35962	34994	1572.2
45	42539	41475	40425	39387	38361	37347	36346	35356	34377	33410	1595.1
46	40927	39864	38814	37776	36751	35738	34737	33748	32770	31803	1617.8
47	39292	38230	37180	36143	35119	34106	33106	32117	31140	30174	1640.3
48	37635	36573	35525	34488	33464	32452	31452	30464	29487	28522	1662.4
49	35956	34895	33847	32811	31787	30776	29777	28789	27813	26848	1684.4
$-10^7\times\frac{dn_{30}}{d\lambda}$	−53.36	52.70	52.07	51.45	50.84	50.24	49.65	49.08	48.51	47.94	
50	1.33 34255	33195	32147	31112	30089	29078	28079	27092	26116	25152	1706.1
51	32532	31472	30426	29391	28369	27358	26360	25374	24398	23434	1727.5
52	30788	29729	28682	27648	26627	25617	24620	23634	22659	21696	1748.9
53	29023	27964	26918	25885	24864	23855	22858	21872	20898	19936	1769.8
54	27237	26179	25133	24101	23080	22072	21075	20090	19117	18155	1790.6
55	25430	24372	23328	22296	21276	20268	19272	18288	17315	16353	1811.4
56	23602	22546	21501	20470	19451	18443	17448	16464	15492	14531	1831.7
57	21754	20698	19655	18624	17605	16599	15604	14621	13649	12689	1851.9
58	19886	18831	17788	16758	15740	14734	13740	12757	11786	10826	1872.0
59	17998	16943	15901	14872	13854	12849	11855	10873	09903	08944	1892.0
60	16090	15036	13994	12965	11948	10944	09951	08970	08000	07041	1911.7

TABLE 7.—*General interpolation table for index of refraction of distilled water*—Con.

t°C	Wave lengths in angstroms										
	5000	5020	5040	5060	5080	5100	5120	5140	5160	5180	5200
0	1.33 74146	73184	72232	71291	70361	69440	68530	67629	66738	65857	64985
1	74119	73157	72206	71265	70335	69414	68504	67604	66713	65832	64960
2	74034	73072	72121	71180	70250	69330	68420	67520	66629	65748	64876
3	73891	72930	71979	71038	70108	69189	68279	67379	66489	65608	64736
4	73694	72733	71782	70842	69912	68993	68083	67183	66293	65412	64541
5	73444	72483	71532	70593	69663	68744	67834	66935	66045	65164	64293
6	73142	72182	71231	70292	69362	68443	67534	66635	65745	64865	63994
7	72791	71830	70880	69941	69012	68093	67184	66285	65396	64516	63645
8	72392	71431	70481	69542	68613	67695	66786	65888	64998	64118	63248
9	71945	70985	70035	69097	68168	67250	66341	65443	64554	63674	62804
$-10^7\times\frac{dn_{10}}{d\lambda}$	=48.26	47.72	47.20	46.67	46.16	45.66	45.16	44.67	44.19	43.73	43.27
10	1.33 71453	70493	69544	68605	67677	66759	65851	64953	64064	63185	62315
11	70917	69957	69008	68070	67142	66224	65316	64418	63530	62651	61782
12	70338	69378	68430	67492	66564	65646	64739	63841	62953	62075	61205
13	69716	68757	67809	66871	65944	65027	64120	63222	62335	61456	60587
14	69054	68096	67148	66210	65283	64366	63460	62563	61675	60797	59929
15	68353	67394	66447	65510	64583	63666	62760	61863	60976	60099	59230
16	67612	66654	65707	64770	63844	62928	62022	61125	60238	59361	58493
17	66834	65877	64930	63993	63067	62151	61246	60350	59463	58586	57718
18	66019	65062	64115	63179	62254	61338	60433	59537	58651	57774	56907
19	65168	64211	63265	62329	61404	60489	59584	58688	57803	56926	56059
20	64282	63325	62379	61444	60519	59604	58699	57804	56919	56043	55177
21	63361	62405	61459	60524	59600	58685	57781	56886	56001	55126	54260
22	62406	61451	60506	59571	58647	57733	56829	55934	55050	54175	53309
23	61419	60464	59519	58585	57661	56747	55844	54950	54066	53191	52325
24	60399	59444	58500	57566	56643	55729	54826	53933	53049	52174	51309
25	59348	58393	57449	56516	55593	54680	53777	52884	52001	51127	50262
26	58265	57311	56367	55434	54512	53599	52697	51804	50921	50048	49183
27	57152	56198	55255	54323	53400	52488	51586	50694	49812	48938	48074
28	56009	55056	54113	53181	52259	51348	50446	49554	48672	47799	46936
29	54837	53884	52942	52010	51089	50178	49276	48385	47503	46631	45768
$-10^7\times\frac{dn_{20}}{d\lambda}$	=47.90	47.36	46.83	46.30	45.79	45.29	44.79	44.30	43.83	43.36	42.90
30	1.33 53636	52683	51742	50810	49889	48978	48078	47187	46306	45434	44571
31	52406	51454	50513	49582	48662	47751	46851	45960	45080	44208	43346
32	51149	50197	49256	48326	47406	46496	45596	44706	43826	42955	42093
33	49864	48913	47973	47043	46123	45214	44314	43425	42545	41674	40813
34	48552	47602	46662	45732	44813	43904	43005	42116	41236	40366	39505
35	47214	46264	45324	44396	43477	42568	41670	40781	39902	39032	38172
36	45850	44900	43961	43032	42114	41206	40308	39420	38541	37672	36812
37	44460	43510	42572	41644	40726	39818	38921	38033	37155	36286	35427
38	43044	42096	41157	40230	39312	38405	37508	36621	35743	34875	34016
39	41604	40656	39718	38791	37874	36967	36071	35184	34307	33439	32580
40	40139	39191	38254	37327	36411	35505	34609	33722	32846	31978	31120
41	38649	37702	36765	35839	34923	34018	33122	32236	31360	30493	29635
42	37136	36189	35253	34327	33412	32507	31612	30726	29850	28984	28127
43	35598	34652	33717	32792	31877	30972	30077	29192	28317	27451	26594
44	34038	33092	32157	31232	30318	29414	28520	27636	26761	25895	25039
45	32454	31509	30574	29650	28736	27833	26939	26055	25181	24316	23460
46	30848	29903	28969	28045	27132	26229	25336	24453	23579	22714	21859
47	29218	28274	27341	26418	25505	24602	23710	22827	21954	21090	20235
48	27567	26624	25690	24768	23856	22954	22062	21180	20307	19443	18589
49	25894	24951	24018	23096	22185	21283	20391	19510	18637	17774	16921
$-10^7\times\frac{dn_{30}}{d\lambda}$	=47.40	46.86	46.33	45.81	45.30	44.81	44.31	43.82	43.35	42.89	42.43
50	1.33 24198	23256	22324	21403	20492	19590	18699	17818	16946	16084	15231
51	22482	21540	20608	19688	18777	17876	16986	16105	15234	14372	13519
52	20743	19802	18871	17951	17041	16141	15251	14371	13500	12639	11787
53	18984	18043	17113	16193	15284	14384	13495	12615	11745	10884	10033
54	17204	16264	15334	14415	13506	12607	11718	10839	09969	09109	08258
55	15403	14463	13534	12616	11707	10809	09920	09042	08173	07313	06462
56	13581	12642	11714	10796	09888	08990	08102	07224	06356	05496	04646
57	11739	10801	09873	08956	08048	07151	06264	05386	04518	03660	02810
58	09877	08939	08012	07095	06189	05292	04405	03528	02661	01803	00954
59	07995	07058	06131	05215	04309	03413	02527	01650	00783	•99926	•99078
60	06094	05157	04231	03315	02409	01514	00628	•99753	•98886	•98029	•97181

TABLE 7.—*General interpolation table for index of refraction of distilled water*—Con.

t°C	Wave lengths in angstroms										$-10^7\times\frac{dn}{d\lambda}$ (λ=5400 A)
	5200	5220	5240	5260	5280	5300	5320	5340	5360	5380	
0	1.33 64985	64122	63268	62423	61586	60758	59939	59127	58324	57529	[−6.8]
1	64960	64097	63243	62398	61562	60734	59915	59104	58301	57506	62.6
2	64876	64014	63160	62315	61479	60652	59832	59021	58218	57424	110.2
3	64736	63874	63020	62176	61340	60512	59693	58883	58080	57285	165.8
4	64541	63679	62826	61981	61146	60318	59500	58689	57887	57092	219.0
5	64293	63431	62578	61734	60899	60072	59253	58443	57641	56846	271.5
6	63994	63132	62280	61436	60600	59774	58955	58145	57343	56550	321.9
7	63645	62784	61931	61088	60252	59426	58608	57798	56996	56203	370.7
8	63248	62387	61535	60691	59856	59030	58212	57403	56602	55808	418.0
9	62804	61943	61091	60248	59414	58588	57770	56961	56160	55367	464.0
$-10^7\times\frac{dn_{10}}{d\lambda}$	=43.27	42.81	42.36	41.93	41.50	41.07	40.65	40.25	39.84	39.45	
10	1.33 62315	61454	60603	59760	58926	58100	57283	56474	55673	54880	508.7
11	61782	60921	60070	59227	58393	57568	56751	55942	55142	54349	552.1
12	61205	60345	59494	58652	57818	56993	56177	55368	54568	53776	594.3
13	60587	59728	58877	58035	57202	56377	55560	54752	53952	53160	635.5
14	59929	59069	58219	57377	56544	55720	54904	54096	53296	52504	675.6
15	59230	58371	57521	56680	55847	55023	54207	53400	52600	51809	714.6
16	58493	57634	56784	55944	55111	54288	53472	52665	51866	51075	752.7
17	57718	56860	56010	55170	54338	53514	52699	51892	51094	50303	789.9
18	56907	56049	55200	54359	53528	52705	51890	51083	50285	49495	826.3
19	56059	55201	54353	53513	52682	51859	51044	50238	49440	48650	861.7
20	55177	54319	53471	52631	51800	50978	50164	49358	48560	47771	896.4
21	54260	53402	52554	51715	50885	50063	49248	48444	47646	46857	930.3
22	53309	52452	51604	50766	49936	49114	48300	47496	46699	45910	963.6
23	52325	51469	50622	49783	48953	48132	47319	46514	45718	44929	996.1
24	51309	50454	49607	48768	47939	47118	46306	45501	44705	43917	1028.0
25	50262	49406	48560	47722	46893	46072	45260	44456	43661	42873	1059.1
26	49183	48328	47482	46645	45816	44996	44184	43381	42586	41798	1089.8
27	48074	47220	46374	45537	44709	43889	43078	42275	41480	40693	1119.9
28	46936	46081	45236	44400	43572	42752	41942	41139	40344	39558	1149.5
29	45768	44914	44069	43233	42405	41586	40776	39974	39180	38393	1178.4
$-10^7\times\frac{dn_{20}}{d\lambda}$	=42.90	42.45	42.00	41.56	41.14	40.72	40.30	39.89	39.49	39.10	
30	1.33 44571	43717	42873	42037	41210	40392	39582	38780	37986	37200	1206.8
31	43346	42493	41649	40814	39987	39169	38359	37558	36764	35979	1234.8
32	42093	41240	40397	39562	38736	37918	37109	36308	35515	34730	1262.4
33	40813	39960	39117	38283	37457	36640	35831	35030	34238	33454	1289.5
34	39505	38654	37811	36977	36152	35335	34527	33726	32934	32150	1316.1
35	38172	37320	36478	35645	34820	34004	33196	32396	31604	30821	1342.3
36	36812	35961	35119	34286	33462	32646	31838	31039	30248	29465	1368.2
37	35427	34576	33735	32902	32078	31263	30456	29657	28866	28083	1393.7
38	34016	33166	32325	31493	30669	29854	29048	28250	27459	26677	1418.7
39	[illegible]	31731	30890	30059	29236	28421	27615	26817	26027	25245	1443.5
40	[illegible]	30271	29431	28600	27777	26963	26158	25360	24570	23789	1467.8
41	[illegible]	28787	27947	27117	26294	25481	24676	23879	23090	22309	1491.9
42	[illegible]	27279	26440	25610	24788	23975	23170	22374	21585	20804	1515.7
43	[illegible]	25747	24908	24079	23258	22445	21641	20845	20057	19276	1539.2
44	[illegible]	24192	23354	22525	21704	20892	20088	19292	18505	17725	1562.3
45	23460	22614	21776	20948	20127	19316	18512	17717	16930	16151	1585.2
46	21859	21013	20176	19348	18528	17717	16914	16119	15333	14554	1607.8
47	20235	19390	18553	17725	16906	16095	15293	14499	13713	12935	1630.2
48	18589	17744	16908	16081	15262	14452	13650	12856	12070	11293	1652.3
49	16921	16076	15241	14414	13596	12786	11985	11192	10406	09629	1674.1
$-10^7\times\frac{dn_{30}}{d\lambda}$	=42.43	41.98	41.53	41.11	40.68	40.25	39.83	39.43	39.04	38.64	
50	1.33 15231	14387	13552	12726	11908	11099	10298	09505	08720	07944	1695.7
51	13519	12676	11841	11016	10198	09390	08589	07797	07013	06237	1717.1
52	11787	10944	10110	09284	08468	07659	06860	06068	05284	04508	1738.3
53	10033	09190	08357	07532	06716	05908	05109	04318	03534	02759	1759.2
54	08258	07416	06583	05759	04943	04136	03337	02546	01764	00989	1780.0
55	06462	05621	04789	03965	03150	02343	01545	00755	*99972	*99198	1800.6
56	04646	03806	02974	02151	01336	00530	*99732	*98942	*98161	*97387	1820.9
57	02810	01970	01138	00316	*99502	*98696	*97899	*97110	*96329	*95556	1841.1
58	00954	00114	*99283	*98461	*97648	*96842	*96046	*95257	*94477	*93704	1861.1
59	1.32 99078	98238	97408	96586	95773	94969	94173	93385	92604	91832	1880.9
60	97181	96343	95513	94692	93880	93076	92280	91492	90713	89941	1900.5

TABLE 7.—*General interpolation table for index of refraction of distilled water*—Con.

t°C	Wave lengths in angstroms					
	5400	5420	5440	5460	5480	5500
0	1.33 56742	55962	55190	54425	53668	52917
1	56718	55939	55167	54402	53645	52895
2	56637	55857	55086	54321	53564	52814
3	56498	55719	54948	54184	53427	52677
4	56306	55527	54755	53992	53235	52486
5	56060	55282	54510	53747	52990	52241
6	55763	54985	54214	53451	52694	51946
7	55417	54639	53868	53105	52349	51600
8	55022	54244	53474	52711	51956	51207
9	54581	53804	53034	52271	51516	50768
$-10^7\times\frac{dn_\lambda}{d\lambda}$	=39.06	38.68	38.30	37.93	37.57	37.22
10	1.33 54095	53318	52548	51785	51030	50282
11	53564	52787	52018	51256	50501	49753
12	52991	52214	51445	50683	49929	49182
13	52376	51600	50831	50069	49315	48568
14	51720	50944	50176	49414	48661	47914
15	51025	50250	49481	48720	47967	47220
16	50292	49516	48748	47988	47234	46488
17	49520	48745	47977	47217	46464	45719
18	48712	47937	47170	46410	45658	44912
19	47868	47094	46326	45567	44815	44070
20	46989	46215	45448	44689	43937	43193
21	46076	45302	44536	43777	43025	42281
22	45128	44355	43589	42831	42080	41336
23	44149	43376	42610	41852	41101	40358
24	43136	42364	41599	40841	40091	39348
25	42093	41321	40556	39799	39049	38306
26	41018	40246	39482	38725	37976	37233
27	39914	39142	38378	37622	36872	36130
28	38779	38008	37244	36488	35739	34998
29	37615	36844	36081	35325	34577	33836
$-10^7\times\frac{dn_\lambda}{d\lambda}$	=38.71	38.33	37.95	37.58	37.22	36.87
30	1.33 36422	35652	34889	34134	33386	32645
31	35201	34432	33669	32914	32167	31426
32	33953	33183	32421	31667	30920	30180
33	32677	31908	31146	30392	29645	28906
34	31374	30605	29844	29091	28344	27605
35	30045	29276	28516	27763	27017	26278
36	28689	27922	27162	26409	25663	24925
37	27308	26541	25781	25029	24284	23546
38	25902	25135	24376	23624	22880	22142
39	24471	23705	22946	22194	21450	20713
40	23015	22250	21491	20740	19996	19260
41	21536	20770	20012	19262	18518	17782
42	20032	19267	18509	17759	17016	16281
43	18504	17740	16983	16233	15491	14756
44	16954	16189	15433	14684	13942	13207
45	15380	14616	13860	13111	12370	11636
46	13783	13020	12264	11516	10775	10041
47	12164	11401	10646	09899	09158	08425
48	10523	09761	09006	08259	07519	06786
49	08860	08098	07344	06597	05857	05125
$-10^7\times\frac{dn_\lambda}{d\lambda}$	=38.25	37.87	37.50	37.14	36.78	36.43
50	1.33 07175	06414	05660	04914	04174	03442
51	05468	04708	03954	03208	02470	01738
52	03741	02980	02228	01482	00744	00013
53	01992	01232	00480	*99735	*98997	*98267
54	00222	*99463	*98711	*97967	*97230	*96500
55	1.32 98432	97673	96922	96178	95441	94712
56	96621	95863	95112	94369	93632	92904
57	94790	94032	93282	92539	91803	91075
58	92939	92182	91432	90690	89954	89226
59	91068	90311	89562	88820	88085	87358
60	89177	88421	87672	86931	86197	85470

TABLE 7.—*General interpolation table for index of refraction of distilled water*—Con.

t°C	Wave lengths in angstroms										$-10^7\times\frac{dn}{d\lambda}$ (λ=6000 A)
	5500	5550	5600	5650	5700	5750	5800	5850	5900	5950	
0	1.33 52917	51073	49271	47510	45788	44103	42455	40842	39262	37714	[−12.4]
1	52895	51051	49250	47489	45767	44083	42436	40823	39243	37696	46.8
2	52814	50971	49170	47410	45688	44005	42358	40746	39167	37620	104.0
3	52677	50834	49034	47274	45554	43871	42224	40612	39034	37488	159.2
4	52486	50643	48843	47084	45364	43682	42036	40424	38847	37301	212.7
5	52241	50399	48600	46841	45122	43440	41795	40184	38607	37062	264.3
6	51946	50104	48306	46547	44829	43148	41503	39893	38316	36772	314.4
7	51600	49760	47962	46204	44486	42806	41162	39552	37976	36432	363.0
8	51207	49367	47570	45813	44096	42416	40772	39164	37588	36045	410.0
9	50768	48928	47131	45375	43658	41979	40337	38728	37154	35611	455.7
$-10^7\times\frac{dn_{10}}{d\lambda}$	−37.22	36.35	35.52	34.72	33.94	33.20	32.50	31.81	31.16	30.52	
10	1.33 50282	48444	46648	44892	43176	41498	39856	38248	36674	35133	500.2
11	49753	47915	46120	44365	42650	40972	39331	37724	36151	34610	543.4
12	49182	47344	45550	43796	42081	40404	38764	37158	35585	34045	585.4
13	48568	46732	44938	43185	41471	39794	38155	36549	34978	33438	626.3
14	47914	46078	44285	42533	40820	39144	37505	35901	34330	32791	666.2
15	47220	45386	43593	41842	40129	38455	36816	35213	33643	32105	705.1
16	46488	44654	42863	41112	39400	37727	36089	34486	32917	31380	743.0
17	45719	43885	42095	40345	38634	36961	35324	33722	32154	30617	779.9
18	44912	43080	41290	39541	37831	36159	34523	32922	31354	29818	815.1
19	44070	42238	40449	38701	36992	35321	33686	32086	30519	28984	851.4
20	43193	41362	39574	37826	36118	34448	32814	31214	29648	28114	883.9
21	42281	40451	38664	36917	35210	33541	31907	30309	28744	27211	919.7
22	41336	39507	37721	35975	34269	32600	30968	29370	27806	26274	952.7
23	40358	38530	36744	35000	33294	31626	29995	28398	26835	25304	985.2
24	39348	37520	35736	33992	32288	30621	28990	27394	25832	24302	1018.9
25	38306	36480	34696	32954	31250	29584	27954	26359	24798	23268	1048.0
26	37233	35408	33626	31884	30181	28516	26887	25293	23733	22204	1078.5
27	36130	34306	32525	30784	29082	27418	25790	24197	22637	21110	1108.4
28	34998	33174	31394	29654	27953	26290	24663	23071	21512	19986	1137.8
29	33836	32014	30234	28495	26795	25133	23507	21916	20358	18833	1166.6
$-10^7\times\frac{dn_{20}}{d\lambda}$	−36.87	36.00	35.17	34.37	33.60	32.86	32.15	31.47	30.82	30.19	
30	1.33 32645	30824	29045	27307	25608	23947	22322	20732	19176	17651	1194.9
31	31426	29606	27828	26092	24394	22734	21110	19520	17965	16441	1222.8
32	30180	28360	26584	24848	23151	21492	19869	18281	16726	15203	1250.3
33	28906	27088	25312	23577	21882	20223	18602	17014	15460	13938	1277.2
34	27605	25788	24014	22280	20585	18928	17307	15721	14168	12647	1303.7
35	26278	24462	22689	20956	19262	17606	15986	14401	12849	11329	1329.9
36	24925	23110	21338	19606	17913	16258	14639	13055	11504	09985	1355.6
37	23546	21732	19961	18230	16539	14885	13267	11684	10134	08616	1381.0
38	22142	20330	18559	16830	15139	13486	11869	10287	08738	07222	1406.0
39	20713	18902	17132	15404	13714	12062	10447	08866	07318	05802	1430.6
40	19260	17449	15681	13954	12265	10615	09000	07420	05873	04358	1455.0
41	17782	15973	14206	12479	10792	09142	07529	05950	04404	02890	1478.9
42	16281	14472	12706	10981	09295	07646	06034	04456	02911	01399	1502.5
43	14756	12948	11184	09459	07774	06127	04515	02938	01395	*99883	1526.0
44	13207	11401	09637	07914	06230	04584	02973	01398	*99855	*96345	1549.1
45	11636	09831	08068	06346	04663	03018	01409	*99834	*98293	*96783	1571.9
46	10041	08238	06476	04755	03074	01430	*99821	*98248	*96707	*95199	1594.3
47	08425	06622	04862	03142	01462	*99818	*98211	*96639	*95100	*93592	1616.6
48	06786	04985	03225	01507	*99827	*98185	*96579	*95008	*93470	*91964	1638.7
49	05125	03325	01567	*99849	*98171	*96530	*94925	*93355	*91818	*90313	1660.4
$-10^7\times\frac{dn_{30}}{d\lambda}$	−36.43	35.56	34.73	33.94	33.17	32.43	31.73	31.05	30.40	29.77	
50	1.33 03442	01644	*99887	*98170	*96493	*94854	*93250	*91681	*90145	*88641	1682.0
51	01738	*99941	*98185	*96470	*94794	*93155	*91553	*89985	*88450	*86947	1703.4
52	00013	*98217	*96462	*94748	*93073	*91436	*89834	*88267	*86734	*85232	1724.4
53	1.32 98267	96472	94718	93005	91332	89695	88095	86529	84997	83496	1745.3
54	96500	94706	92953	91242	89569	87934	86335	84770	83239	81739	1766.1
55	94712	92919	91168	89458	87786	86152	84554	82990	81460	79962	1786.5
56	92904	91112	89362	87653	85983	84350	82753	81190	79661	78164	1806.8
57	91075	89284	87536	85828	84159	82527	80932	79370	77842	76346	1826.9
58	89226	87437	85690	83983	82315	80685	79090	77530	76003	74508	1846.8
59	87358	85570	83824	82118	80451	78822	77229	75670	74144	72650	1866.6
60	85470	83683	81938	80234	78568	76940	75348	73790	72265	70772	1886.3

TABLE 7.—*General interpolation table for index of refraction of distilled water*—Con.

t°C	Wave lengths in angstroms										
	6000	6050	6100	6150	6200	6250	6300	6350	6400	6450	6500
0	1.33 36197	34710	33252	31821	30417	29038	27684	26354	25046	23761	22497
1	36180	34693	33235	31805	30401	29023	27670	26340	25033	23749	22485
2	36104	34618	33161	31731	30328	28950	27598	26268	24962	23678	22415
3	35972	34487	33030	31601	30198	28822	27469	26141	24835	23551	22289
4	35786	34302	32845	31417	30015	28638	27287	25959	24654	23371	22109
5	35548	34064	32608	31180	29779	28403	27052	25724	24420	23138	21877
6	35258	33775	32320	30892	29492	28116	26766	25439	24136	22854	21594
7	34920	33437	31982	30556	29156	27781	26431	25105	23802	22521	21261
8	34533	33051	31597	30171	28772	27398	26049	24723	23421	22140	20882
9	34100	32618	31165	29740	28341	26968	25620	24295	22993	21714	20456
$-10^7\times\frac{dn_{10}}{d\lambda}$	=29.92	29.33	28.77	28.23	27.70	27.20	26.72	26.25	25.80	25.36	24.94
10	1.33 33622	32141	30689	29264	27866	26494	25146	23822	22521	21242	19984
11	33100	31620	30168	28744	27347	25975	24628	23305	22005	20727	19470
12	32536	31056	29605	28182	26786	25415	24068	22746	21446	20169	18913
13	31930	30451	29001	27578	26183	24812	23467	22145	20846	19570	18314
14	31283	29805	28356	26934	25539	24170	22825	21504	20206	18930	17676
15	30598	29120	27672	26251	24857	23488	22144	20824	19527	18252	16998
16	29874	28397	26950	25529	24136	22768	21425	20106	18809	17535	16282
17	29112	27636	26190	24770	23378	22011	20668	19350	18054	16780	15528
18	28314	26839	25393	23975	22583	21217	19875	18557	17262	15990	14738
19	27480	26006	24561	23143	21752	20387	19046	17729	16435	15163	13913
20	26612	25138	23694	22277	20887	19522	18183	16866	15573	14302	13052
21	25709	24236	22793	21377	19988	18624	17285	15970	14677	13407	12158
22	24772	23301	21858	20443	19055	17692	16354	15039	13748	12478	11230
23	23803	22333	20891	19477	18089	16727	15390	14076	12786	11517	10270
24	22802	21333	19892	18478	17092	15731	14394	13082	11792	10524	09278
25	21770	20301	18861	17449	16063	14703	13367	12055	10766	09500	08254
26	20707	19239	17800	16388	15003	13644	12309	10998	09710	08444	07200
27	19613	18146	16708	15297	13914	12555	11221	09911	08624	07359	06116
28	18490	17024	15587	14177	12794	11437	10104	08795	07508	06244	05002
29	17338	15873	14437	13028	11646	10289	08957	07649	06364	05100	03859
$-10^7\times\frac{dn_{20}}{d\lambda}$	=29.50	28.99	28.43	27.89	27.37	26.87	26.38	25.92	25.47	25.03	24.62
30	1.33 16157	14693	13258	11850	10469	09113	07782	06475	05190	03928	02687
31	14948	13485	12051	10644	09264	07909	06579	05272	03989	02728	01488
32	13712	12249	10816	09410	08031	06677	05348	04042	02760	01500	00260
33	12448	10987	09554	08149	06771	05418	04090	02786	01504	00244	*99006
34	11157	09697	08266	06862	05484	04132	02805	01502	00221	*98963	*97725
35	09840	08381	06951	05548	04171	02820	01494	00192	*98912	*97654	*96418
36	08498	07039	05610	04208	02832	01483	00157	*98856	*97577	*96321	*95085
37	07129	05672	04244	02843	01468	00119	*98795	*97494	*96217	*94961	*93727
38	05736	04280	02852	01452	00079	*98731	*97408	*96108	*94831	*93576	*92343
39	04318	02862	01436	00037	*98664	*97318	*95995	*94697	*93421	*92167	*90935
40	02875	01421	*99995	*98597	*97226	*95880	*94559	*93261	*91986	*90734	*89502
41	01408	*99955	*98530	*97133	*95763	*94418	*93098	*91801	*90527	*89276	*88045
42	1.32 99917	98465	97042	95646	94276	92932	91613	90318	89045	87794	86565
43	98403	96952	95529	94134	92766	91423	90105	88810	87539	86289	85061
44	96865	95415	93994	92600	91233	89891	88574	87280	86009	84761	83533
45	95305	93856	92436	91043	89676	88336	87020	85727	84457	83210	81983
46	93722	92274	90855	89463	88098	86758	85443	84151	82882	81636	80410
47	92116	90669	89251	87860	86496	85158	83844	82553	81285	80040	78815
48	90488	89043	87626	86236	84873	83535	82222	80933	79666	78422	77198
49	88839	87394	85978	84590	83228	81891	80579	79291	78025	76782	75559
$-10^7\times\frac{dn_{30}}{d\lambda}$	=29.17	28.58	28.02	27.48	26.96	26.46	25.98	25.52	25.07	24.64	24.22
50	1.32 87168	85724	84309	82922	81561	80225	78914	77627	76362	75120	73899
51	85475	84032	82619	81232	79872	78538	77228	75942	74678	73437	72217
52	83761	82320	80907	79522	78163	76829	75520	74235	72973	71732	70513
53	82026	80586	79174	77790	76432	75100	73792	72508	71247	70007	68789
54	80270	78831	77421	76038	74681	73350	72043	70760	69500	68261	67044
55	78494	77056	75647	74265	72909	71579	70273	68991	67732	66495	65279
56	76698	75261	73852	72471	71117	69788	68483	67202	65944	64708	63493
57	74881	73445	72038	70658	69304	67976	66673	65393	64136	62901	61687
58	73044	71609	70203	68824	67472	66145	64843	63564	62308	61074	59861
59	71187	69754	68348	66971	65620	64294	62993	61715	60460	59227	58016
60	69311	67878	66474	65098	63748	62423	61123	59846	58592	57361	56150

TABLE 7.—*General interpolation table for index of refraction of distilled water*—Con.

t°C	Wave lengths in angstroms										$-10^7\times\frac{dn}{dt}$ (λ=7000 A)
	6500	6550	6600	6650	6700	6750	6800	6850	6900	6950	
0	1.33 22497	21254	20030	18825	17639	16471	15319	14185	13066	11963	[−23.6]
1	22485	21242	20019	18815	17629	16462	15311	14177	13059	11956	35.2
2	22415	21173	19950	18747	17562	16395	15244	14111	12994	11892	92.0
3	22289	21047	19826	18623	17438	16272	15122	13990	12873	11771	148.9
4	22109	20868	19647	18444	17261	16095	14946	13814	12698	11597	200.0
5	21877	20636	19416	18214	17031	15866	14718	13586	12471	11370	251.4
6	21594	20354	19134	17933	16750	15586	14438	13308	12193	11094	301.1
7	21261	20022	18803	17603	16421	15257	14110	12980	11866	10767	349.3
8	20882	19643	18424	17225	16044	14881	13735	12605	11492	10394	396.2
9	20456	19218	18000	16801	15621	14458	13313	12184	11071	09974	441.7
$-10^7\times\frac{dn_{10}}{d\lambda}$	−24.94	24.54	24.15	23.78	23.42	23.06	22.73	22.40	22.09	21.78	
10	1.33 19984	18748	17530	16332	15151	13991	12846	11718	10606	09510	485.7
11	19470	18234	17017	15820	14641	13480	12336	11209	10097	09002	528.7
12	18913	17677	16461	15265	14087	12926	11783	10657	09546	08451	570.5
13	18314	17080	15864	14669	13491	12332	11189	10063	08954	07859	611.2
14	17676	16442	15227	14032	12856	11697	10555	09430	08321	07228	650.8
15	16998	15764	14551	13357	12181	11023	09882	08758	07649	06557	689.4
16	16282	15049	13836	12643	11468	10310	09170	08047	06940	05848	727.1
17	15528	14296	13084	11892	10717	09561	08422	07299	06192	05101	763.9
18	14738	13507	12296	11104	09931	08775	07637	06515	05409	04318	799.8
19	13913	12682	11472	10281	09108	07954	06816	05695	04590	03500	834.9
20	13052	11823	10614	09423	08251	07097	05960	04840	03736	02647	869.2
21	12158	10930	09721	08531	07360	06207	05071	03952	02848	01760	902.8
22	11230	10003	08795	07606	06436	05284	04148	03030	01927	00840	935.7
23	10270	09043	07836	06649	05479	04328	03193	02076	00974	*99888	967.9
24	09278	08052	06846	05659	04490	03340	02206	01089	*99988	*98903	999.4
25	08254	07029	05824	04638	03470	02320	01188	00072	*98972	*97887	1030.4
26	07200	05976	04772	03586	02420	01271	00139	*99024	*97924	*96841	1060.7
27	06116	04892	03689	02505	01339	00191	*99060	*97945	*96847	*95764	1090.4
28	05002	03779	02577	01393	00228	*99081	*97951	*96838	*95740	*94658	1119.6
29	03859	02637	01436	00253	*99089	*97943	*96814	*95701	*94604	*93523	1148.4
$-10^7\times\frac{dn_{20}}{d\lambda}$	−24.62	24.21	23.82	23.45	23.09	22.74	22.40	22.07	21.76	21.46	
30	1.33 02687	01467	00266	*99084	*97921	*96776	*95648	*94536	*93440	*92360	1176.5
31	01488	00268	*99068	*97888	*96725	*95581	*94453	*93343	*92248	*91169	1204.2
32	00260	*99042	*97843	*96663	*95502	*94358	*93232	*92122	*91028	*89950	1231.5
33	1.32 99006	97788	96591	95412	94251	93109	91983	90874	89781	88704	1258.4
34	97725	96508	95312	94134	92974	91832	90708	89600	88508	87431	1284.7
35	96418	95202	94006	92829	91671	90530	89406	88299	87208	86133	1310.7
36	95085	93870	92675	91499	90342	89202	88079	86973	85883	84808	1336.3
37	93727	92513	91319	90144	88987	87848	86726	85621	84532	83458	1361.5
38	92343	91130	89937	88763	87607	86469	85349	84244	83156	82083	1386.4
39	90935	89723	88531	87358	86203	85066	83946	82843	81756	80684	1410.9
40	89502	88291	87100	85928	84774	83638	82519	81417	80331	79260	1435.0
41	88045	86835	85645	84474	83321	82186	81068	79967	78882	77812	1459.0
42	86565	85356	84166	82996	81844	80710	79594	78493	77409	76340	1482.5
43	85061	83853	82664	81495	80344	79211	78096	76996	75913	74845	1505.8
44	83533	82326	81139	79971	78821	77689	76574	75476	74394	73327	1528.7
45	81983	80777	79591	78424	77275	76144	75030	73933	72852	71786	1551.3
46	80410	79206	78020	76854	75706	74576	73464	72367	71287	70222	1573.8
47	78815	77612	76427	75262	74116	72986	71875	70779	69700	68636	1596.0
48	77198	75995	74812	73648	72502	71374	70264	69169	68091	67028	1617.9
49	75559	74357	73175	72012	70868	69741	68631	67538	66460	65398	1639.5
$-10^7\times\frac{dn_{30}}{d\lambda}$	−24.22	23.82	23.43	23.06	22.70	22.35	22.01	21.68	21.37	21.07	
50	1.32 73899	72698	71517	70355	69211	68085	66976	65884	64808	63747	1660.9
51	72217	71017	69837	68676	67533	66408	65301	64210	63134	62075	1682.2
52	70513	69315	68136	66976	65834	64710	63604	62514	61440	60381	1703.2
53	68789	67592	66414	65255	64114	62992	61886	60797	59724	58666	1724.0
54	67044	65848	64671	63513	62374	61252	60147	59059	57987	56931	1744.5
55	65279	64083	62908	61751	60612	59492	58388	57301	56230	55175	1764.9
56	63493	62299	61124	59968	58831	57711	56609	55523	54453	53399	1785.2
57	61687	60494	59320	58166	57029	55911	54810	53725	52656	51603	1805.1
58	59861	58669	57496	56343	55208	54090	52990	51906	50839	49786	1825.0
59	58016	56824	55653	54500	53366	52250	51151	50068	49002	47950	1844.7
60	56155	54960	53790	52638	51505	50390	49292	48210	47145	46095	1864.2

TABLE 7.—*General interpolation table for index of refraction of distilled water*—Con.

	Wave lengths in angstroms										
t°C	7000	7050	7100 (Extrapolated)	7150 (Extrapolated)	7200 (Extrapolated)	7250 (Extrapolated)	7300	7350	7400	7450	7500
0	1.33 10874	09800	08741	07694	06660	05639					
1	10868	09795	08735	07689	06656	05636					
2	10804	09732	08673	07628	06595	05576					
3	10685	09613	08555	07510	06478	05460					
4	10511	09440	08383	07338	06308	05289					
5	10286	09215	08158	07115	06084	05067					
6	10009	08939	07883	06840	05811	04794					
7	09684	08614	07559	06517	05488	04472					
8	09311	08242	07188	06147	05118	04102					
9	08892	07824	06770	05730	04702	03687					
$-10^7\times\frac{dn_{10}}{d\lambda}$	=21.48	21.20	20.93	20.66	20.41	20.16					
10	1.33 08428	07361	06308	05268	04241	03227					
11	07921	06854	05802	04763	03737	02724					
12	07371	06305	05254	04215	03190	02178					
13	06780	05715	04664	03627	02602	01591					
14	06149	05085	04035	02998	01974	00963					
15	05479	04415	03366	02330	01307	00297					
16	04770	03708	02659	01624	00602	*99592					
17	04025	02963	01915	00881	*99860	*98851					
18	03243	02182	01135	00101	*99081	*98073					
19	02426	01365	00319	*99286	*98266	*97260					
20	01573	00514	*99469	*98437	*97418	*96411	*95417	*94434	*93463	*92503	*91553
21	00687	*99629	*98584	*97553	*96535	*95529					
22	1.32 99768	98710	97667	96636	95619	94614					
23	98816	97759	96716	95687	94670	93666					
24	97832	96776	95734	94706	93690	92687					
25	96818	95762	94721	93693	92678	91676					
26	95772	94718	93677	92650	91636	90635					
27	94696	93643	92603	91577	90564	89564					
28	93591	92539	91500	90475	89462	88463					
29	92457	91405	90368	89343	88332	87333					
$-10^7\times\frac{dn_{20}}{d\lambda}$	=21.16	20.87	20.60	20.34	20.09	19.84					
30	1.32 91295	90244	89207	88184	87173	86175					
31	90104	89054	88018	86996	85986	84989					
32	88886	87837	86802	85781	84772	83776					
33	87641	86593	85559	84538	83530	82535					
34	86370	85323	84289	83270	82263	81268					
35	85072	84026	82994	81975	80968	79975					
36	83748	82703	81672	80654	79649	78656					
37	82400	81355	80325	79308	78304	77312					
38	81026	79982	78953	77937	76933	75942					
39	79627	78584	77556	76541	75538	74549					
40	78204	77162	76135	75121	74119	73130					
41	76757	75716	74690	73677	72676	71688					
42	75286	74247	73221	72209	71209	70222					
43	73792	72753	71729	70717	69719	68733					
44	72275	71237	70213	69203	68206	67221					
45	70735	69698	68675	67666	66670	65686					
46	69172	68137	67115	66106	65111	64128					
47	67587	66553	65532	64525	63530	62549					
48	65980	64947	63927	62921	61928	60947					
49	64352	63319	62300	61295	60303	59323					
$-10^7\times\frac{dn_{30}}{d\lambda}$	=20.77	20.49	20.22	19.95	19.70	19.45					
50	1.32 62701	61670	60652	59648	58657	57678					
51	61030	59999	58983	57980	56990	56012					
52	59337	58308	57292	56290	55301	54325					
53	57623	56595	55581	54580	53592	52616					
54	55889	54862	53849	52849	51862	50887					
55	54134	53108	52096	51097	50111	49138					
56	52359	51334	50323	49325	48340	47368					
57	50564	49540	48530	47533	46550	45579					
58	48749	47726	46717	45722	44739	43769					
59	46914	45892	44885	43890	42909	41940					
60	45060	44039	43032	42039	41059	40091					

In table 7 the values of the derivatives at specified coordinates have been computed principally from the mean first differences of adjacent listings, but third differences have not been neglected where they affect the derivatives appreciably. For the checking of many of the temperature derivatives and for computing all of those at and near 0° C, the equation

$$\left(\frac{dn}{dt}\right)_\lambda = \frac{(n_{20}-n_t)_\lambda - 10^{-7}\{3\overline{B}_\lambda(\Delta t)^2+2\overline{A}_\lambda\Delta t+\overline{C}_\lambda\}}{t+\overline{D}} \quad (5)$$

was derived from eq 2.

As a check on the consistency of the various index computations, all data in tables 5, 6, and 7 were redifferenced after tabulation. Efforts have been made to secure computational correctness within $\pm 1\times 10^{-7}$, chiefly for differential purposes among tabulated values, but also in order that interpolations within a few units of the seventh decimal place can be made. Therefore, these tables provide an adequate basis for further studies of the refractivity of water by interferometric methods,[28] and they greatly facilitate such procedures by obviating the necessity of first using inconveniently thin films.

2. TEMPERATURE OF MAXIMUM INDEX

It will be noticed in table 7 that the value of the temperature coefficient, $(dn/dt)_\lambda$, is usually negative, increases continuously as the temperature is reduced, and for the longer wave lengths passes through zero and becomes positive at some temperature between +1° C and 0° C. Such positive values are enclosed in brackets. Where $(dn/dt)_\lambda$ becomes zero, the value of n_λ is a maximum. The corresponding temperature increases with the wave length, lying above 0° C if λ exceeds a value somewhere around 4600 A. This last is in conflict with the observations reported by Damien, Ketteler, Pulfrich, and more recently by Gregg-Wilson and Wright, all of whom found that the maximum index for the sodium lines lay below 0° C.[29] On the contrary, one may deduce from Conroy's data a slightly positive value for the temperature of maximum index for the sodium lines; and L. Lorenz, who alone of all previous observers determined t_{max} for more than one wave length, found that the maximum lay slightly above 0° C for sodium light and at a decidedly higher temperature for lithium light.

In figure 12 most of these data are compared. Points upon the author's curve for the relative index were obtained by setting the right-hand member of eq 5 equal to zero and solving for t for each of several wave lengths. The corresponding curve for the absolute index, $\bar{n}$, was also computed,[30] because it is believed that the Lorenz data are probably referred to a vacuum.

Damien's work, which seems carefully done, indicates a temperature of maximum index considerably lower than any included in

[28] See remarks and references in BS J. Research 2, 916 (1929) RP64.

[29] For references, see table 1 in section I-2.

[30] The right-hand member of the equation $\left(\frac{d\bar{n}}{dt}\right)_\lambda = \mu\left(\frac{dn}{dt}\right)_\lambda + n_\lambda\left(\frac{d\mu}{dt}\right)$ was equated to zero after combination with eq 5. Approximate maximal values of n_λ and the well-known values of μ and of $\left(\frac{d\mu}{dt}\right)$ for air were used. For each of several wave lengths the resulting equations were solved for t.

figure 12. These widely varying results, as well as the great divergence among values of dn/dt (see fig. 6) that are found by various investigators for temperatures at and near 0° C, suggest that the conditions of measurement are not comparable for the several observers.[31] If time itself is not an important factor in the attainment of equilibrium at and below 0° C, perhaps the condition that does obtain is dependent, not only directly but in some indirect and important manner, on some slowly changing condition such, for example, as the amount of dissolved glass or metal. Certainly, in these experiments there was, at 0° C, a slight progressive trend toward a lower rather than a higher index as the time of holding in the prism was extended (see section VI, 3 and 4). The magnitude of this change was small but perhaps as large as 1×10^{-6} within the first 2 or 3 hours of elapsed time.

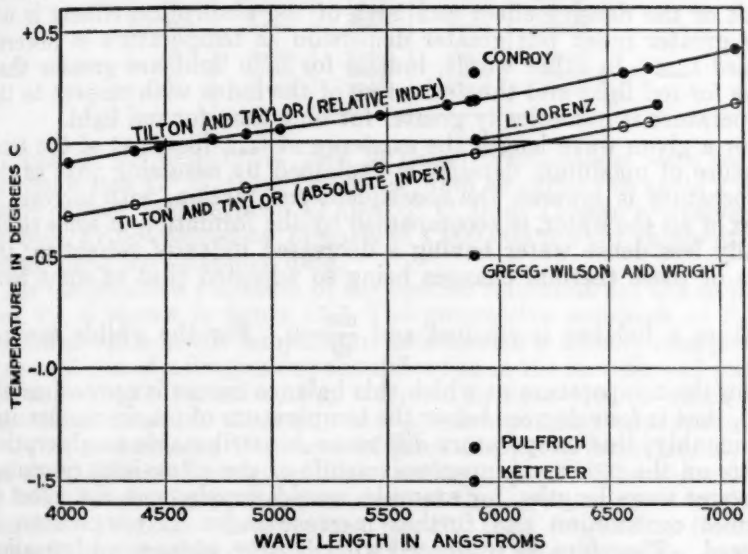

FIGURE 12.—*Temperature of maximum index of distilled water as a function of wave length.*

In considering the temperature of maximum index as a function of wave length, it is useful to recall the concept that refractive index for the visible region of the spectrum consists primarily of an effect that is independent of wave length and corresponds in some cases to the square root of the dielectric constant, plus the dispersive effects of absorption bands in the infrared and in the ultraviolet regions.

[31] In some instances it is, of course, possible that values of dn/dt at 0° C are seriously affected by the type of function that is selected and by the care used in curve fitting, especially when no observations are made on undercooled water. For example, consider eq 11, 12, and 13 on page 208, J. Research NBS 18 (1937), all adjusted by least squares for the D-lines indices of the isothermally adjusted system (see section IV-2-a, this paper). The 4-constant eq 11, being very similar to a reduced form of the general interpolation formula (see eq 3, this paper), yields for t_{max} a value of +0.15 in fair agreement with +0.19° C as plotted in figure 12, this paper. On the other hand, from eq 12, a 4-constant power series in t, one derives the especially discordant value −0.18; and from eq 13, a 6-constant power series, the poor value −0.02° C. It seems, however, that a power series may be satisfactory for this computation if sufficient terms are used, because a 7-term power series, adjusted to fit exactly the approved computed data of this paper at 0, 10, 20, 30, 40, 50, and 60° C yielded a value of t_{max}=+0.17 in excellent agreement with the +0.19° C of figure 12.

Goodness of fit is imperative even for data on water at temperatures below 0° C. Pulfrich's data, for example, yield values of −0.34 or −1.35° C for t_{max} according as one uses the power series given in the Landolt-Börnstein Tabellen (vol. 2, p. 957, 5th ed.) or the similar but much better fitting formula given on page 87 in Dufet's Recueil de Donees Numeriques Optiques, Paris, 1900.

Although temperature changes in density affect index through both the constant term and the dispersive or absorption terms, the total of such increments in index arising from the former are, for fairly transparent substances, so much the more important that it is often convenient and useful to consider temperature changes in index as essentially (1) a density effect, approximately constant for all wave lengths, and (2) absorption band effects that are in some cases very different in magnitude at opposite ends of the visible region. Absorption in the infrared decreases index in the visible region more for red than for blue light. Absorption in the ultraviolet increases index more for blue than for red light. Consequently, both these absorption effects produce normal dispersion in the visible region and their relative importance can be estimated by considering partial dispersions in widely different wave-length regions and noting the trends of the partial dispersions with changes in temperature. For water the net combined result of the density effect and both of the absorption effects is not only greater index but greater dispersion as temperature is lowered toward t_{max}. In other words, indices for blue light are greater than those for red light and the derivative of the index with respect to the temperature is numerically greater for blue than for red light.

For a given wave length the existence of t_{max}, like that of the temperature of maximum density, is explained by assuming that as the temperature is lowered the consequent contraction, with increase in index of all the water, is accompanied by the formation of some structurally less dense water having a decreased index of refraction; the rates of these thermal changes being so adjusted that at some temperature a balance is effected and $\frac{dn}{dt}=0$. For the visible spectral region the temperature at which this balance occurs is approximately 0° C, that is four degrees below the temperature of maximum density. Presumably, this temperature difference is attributable to absorption effects on the index. A progressive shift of the ultraviolet resonance to longer wave lengths, for example, would supplement the effect of thermal contraction and further increase index as temperature is lowered. Therefore, as compared with density, more rapid formation of the structurally open water, and consequently a lower temperature, is required to effect a balance for the index changes. Since the absorption bands have an appreciably different effect on index for different portions of the visible spectrum it is evident that the temperature of maximum index should, in general, be a function of wave length. For water it may be concluded from figure 10 in section IV–2–a that, effectively, both the ultraviolet and the infrared bands move toward the visible region as the temperature is lowered below 20° C. Consequently, the indices for red light would increase less rapidly than those for blue light and it is not surprising that t_{max} is found somewhat higher for red light.

3. SPECIFIC REFRACTION

The Lorenz-Lorentz specific refraction,

$$P=\frac{n^2-1}{n^2+2}\cdot\frac{1}{d},$$

was computed for several temperatures and a few wave lengths, both for absolute and for relative indices, those for the latter being listed in table 8 for ready reference.

TABLE 8.—*Specific refraction of distilled water*

$\left[\bar{P}=\frac{n^2-1}{n^2+2}\cdot\frac{1}{d}\text{ in milliliters per gram}\right]$

t°C	λ=6563 A	λ=5893 A	λ=4861 A	λ=4358 A
0	0.205214	0.206254	0.208585	0.210317
5	.205155	.206193	.208520	.210250
10	.205103	.206138	.208463	.210191
15	.205058	.206092	.208414	.210142
20	.205020	.206053	.208372	.210099
25	.204989	.206020	.208336	.210063
30	.204963	.205991	.208307	.210034
35	.204942	.205969	.208282	.210010
40	.204925	.205951	.208264	.209991
45	.204913	.205937	.208249	.209976
50	.204904	.205928	.208239	.209967
55	.204900	.205922	.208233	.209960
60	.204898	.205919	.208229	.209957

Values of the density, d, used in these computations were taken, between 0 and 42° C, from Chappuis' data as revised in table 2 of a former paper,[32] and between 42 and 60° C, from Thiesen's [33] values as modified, by not exceeding 13 parts in 1,000,000 toward values extrapolated from the Chappuis data.

The temperature variation of the specific refraction for the sodium lines, P_D, is shown in figure 13. The progressive approach of P_D to a constant value as the temperature is increased is usually interpreted as an evidence of a progressive simplification in the structure of water. The wave-length variation, P_{20}, is shown in figure 14, to which has been added (crosses) the value of P_{20}, corresponding approximately to $\lambda=\infty$, as estimated from each of three dispersion formulas, 13, 14, and 17, that have been given in an earlier paper.[34] The value of n^2 for $\lambda=\infty$ is simply assumed as that of the constant term in those formulas. Of these three values for n^2_∞ that (a^2_{13}) from formula 13 would presumably give the best value if the dispersion can be satisfactorily represented by two Sellmeier terms. However, figure 14 indicates a much lower value, one at least as low as those given by the other two formulas which correspond to expanded forms of the Ketteler-Helmholtz equation. This accords with the known existence of many absorption bands in the infrared and confirms the view that the simple expansion is not limited to the effect of a single band, but gives an approximation to the effect arising from many bands.

Other commonly used expressions for specific refraction, such as $\frac{n-1}{d}$ and $\frac{n^2-1}{d}$, are similar in some respects to the Lorenz-Lorentz form but for water are subject to larger percentage variations over

[32] J. Research NBS 18, 213 (1937) RP971.
[33] Wiss. Abhandl. physik. tech. Reichsanstalt 4, 30 (1904).
[34] See formulas 13, 17, and 14 in RP934, J. Research NBS 17 (1936). Equations 5 of that paper show how formulas 17 and 14 may be viewed as approximations suitable for the case in which many absorption bands exist in the infrared region.

given temperature intervals. Eykman's [35] form $\frac{n^2-1}{n+0.4}\cdot\frac{1}{d}$, which he considered superior for many organic liquids, is for water actually less constant than that of Lorenz-Lorentz.

Since the Lorenz P is sometimes [36] written as $\frac{n^2-1}{n^2+x}\cdot\frac{1}{d}$, where x is expected to have slightly different values for various substances, the possibility of improving the constancy by arbitrarily using some value of x other than 2 was cursorily investigated. Such an arbitrary pro-

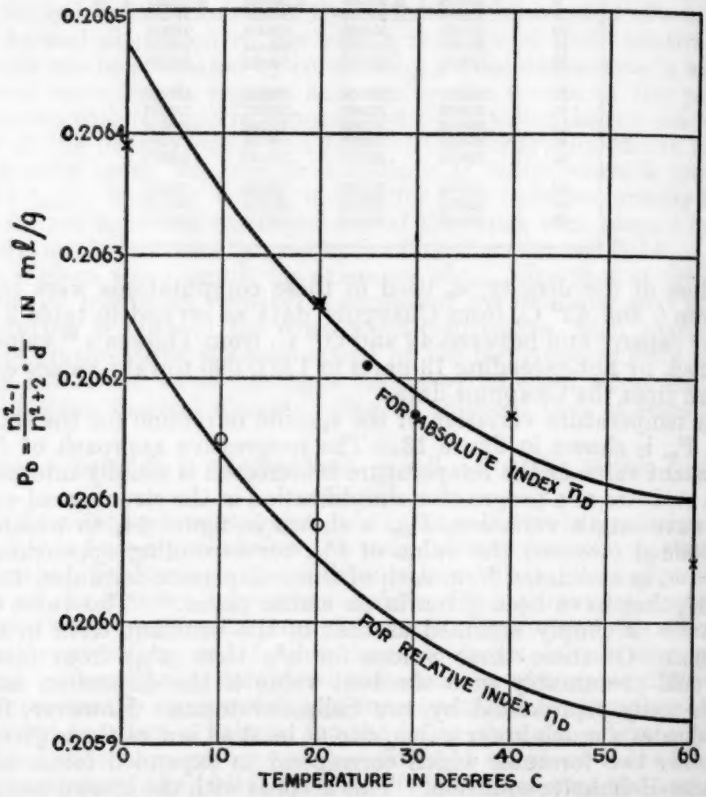

FIGURE 13.—*Specific refraction of distilled water for various temperatures.*

The curves represent the present work; circles, crosses, and dots show values listed, respectively, by L. Lorenz, by E. Flatow (one correction), and by Baxter, Burgess, and Daudt.

cedure yields different results when attention is confined to different temperature intervals. For example, from 0 to 40° C a value of approximately 0.6 is found, while for the range 0 to 60°, 1.1 is a more

[35] J. F. Eykman. Rec. trav. chim. **14**, 193 (1895).

[36] In the H. A. Lorentz notation (The Theory of Electrons, p. 137–139, 2d ed., Teubner, Leipzig, 1916), $x=\frac{1}{a+s}-1$, where a is a constant little different from one-third and s is for each medium a constant difficult to determine but one that was expected to be approximately zero for isotropic bodies in general, such as glass, liquids, and gases. Experimentally, however, values of x differing very appreciably from the value 2 have been found. See, for example, E. Ketteler, Ann. Physik [Wied] **30**, 288 (1887) and **33**, 358 (1888), who computed values of x for numerous liquids and lists some values larger than 4.

suitable value. For the range 0 to 100° C, however, it appears that the customarily used value, $x=2$, is approximately an optimum.

4. PARTIAL DISPERSIONS

Precise data on the dispersion of water at various temperatures are desirable for use in calibrating precision refractometers. Dis-

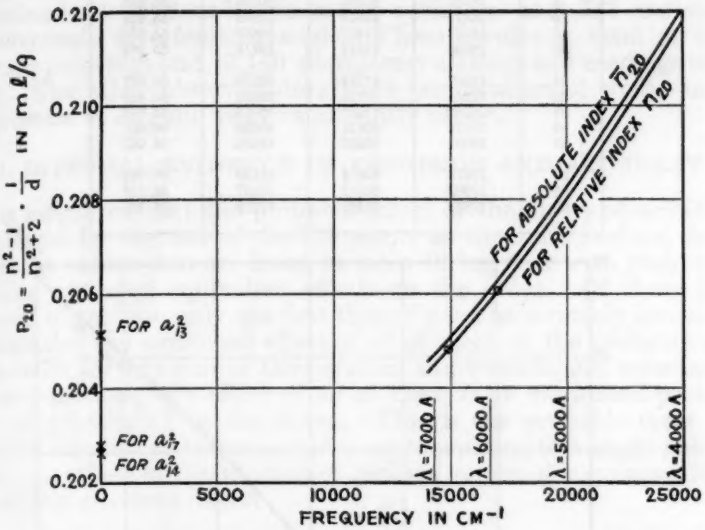

FIGURE 14.—*Specific refraction of distilled water for various frequencies.*

The curves represent the present work; circles show values listed by L. Lorenz. Crosses indicate values of P_{20} for approximate estimates of n_∞ that are furnished by values of the constant a^2 in various forms of the Ketteler-Helmholz dispersion formulas (see text).

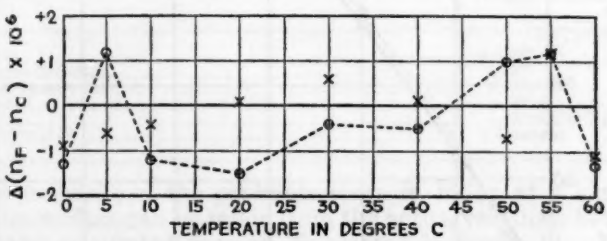

FIGURE 15.—*Comparison between observed and computed values of partial dispersion* $(n_F - n_C)$ *for distilled water.*

The line $\Delta(n_F - n_C)=0$ represents data computed by the general interpolation formula (see eq 3). Circles and dotted line show observed values. Crosses indicate isothermally adjusted data. Here n_F and n_C are values of the index for the *F* and *C* lines of hydrogen, respectively.

persion data yielded by these experiments are given in table 9, and figure 15 is drawn to show how closely these partial dispersions (obtained by differencing table 5, or in other words, computed by use of the general interpolation formula, see eq 3) agree with the observed data.

TABLE 9.—*Partial dispersions of distilled water*

[For wave-length designations see table 3]

t°C	$10^7(n_D-n_C)$	$10^7(n_F-n_D)$	$10^7(n_F-n_C)$	$\nu=\frac{n_D-1}{n_F-n_C}$
0	18554	41636	60190	55.482
5	18516	41583	60098	55.556
10	18471	41516	59986	55.628
15	18420	41437	59857	55.697
20	18366	41349	59714	55.763
25	18307	41252	59559	55.827
30	18246	41148	59394	55.888
35	18182	41038	59219	55.946
40	18115	40922	59036	56.001
45	18046	40800	58846	56.053
50	17976	40674	58650	56.102
55	17903	40543	58447	56.148
60	17830	40409	58238	56.191

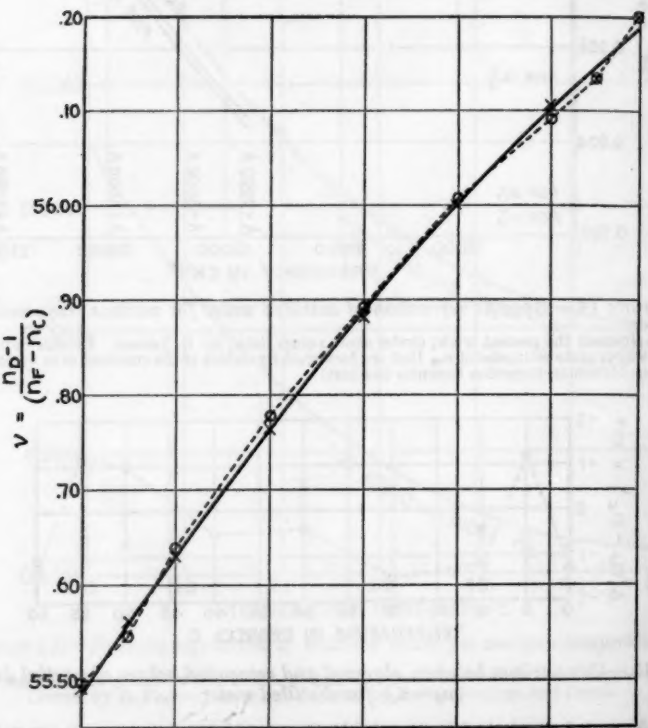

FIGURE 16.—*Abbe's ν-value, or constringence, of distilled water as a function of temperature.*

The continuous line represents data computed by the general interpolation formula (see eq 3). Circles and dotted line show observed values. Crosses indicate isothermally adjusted data.

In figure 16 the observed and computed values of $\nu=\frac{n_D-1}{n_F-n_C}$ are compared. This reciprocal measure of dispersion, or constringence

as it has been called, increases with the temperature at the rate of 0.015 per degree centigrade for temperatures near 0° C, and at the rate 0.009 for temperatures near 60° C.

VI. SUPPLEMENTARY DISCUSSION

The data given in this paper depend directly on 2,538 individual determinations of double minimum deviation and 747 individual measurements of refracting angle. These involve a total of 6,570 telescope pointings and 13,140 micrometer settings and readings of the circle. The other observed data were temperature of water and of air, pressure of air, and relative humidity of air.

1. INTERNAL EVIDENCE OF PRECISION AND ACCURACY

It is estimated that the probable errors of the direct observations, as averaged for any one of the 133 points on the index surface, do not exceed the values that are listed in table 10 together with their corresponding averaged equivalent effects on the index. Of these listed observed quantities, only the first three [37] need be seriously considered in estimating the combined effect of all of them on the probable error of the index for any pair of temperature and wave-length coordinates. The root-mean-square effect of all of them is an estimated probable error of $\pm 6.6 \times 10^{-7}$ in the index. This is the probable error that would be expected in the mean index corresponding to a single point on the index surface in the absence of residual errors of a systematic but not entirely constant nature.

TABLE 10.—*Estimated precision of directly observed data for a point on the index surface*

Observed quantity	Estimated probable error of mean	(Averaged) equivalent $\Delta n \times 10^7$
Refracting angle	±0.20″	4.1
Double minimum deviation	±.20″	5.1
Temperature of water	±.001° C	0.9
Temperature of air	±.05° C	.1
Pressure of air	±.05 mm of Hg	.2
Relative humidity of air	±5 percent	.3

Another estimate of the probable error in index at a single point on the index surface can be made from the actual residuals between the observed and computed indices, as plotted in figure 11. Using the formula P. E. $= \pm 0.6745 \sqrt{\Sigma r^2/C}$, where $\Sigma r^2 = 337.1 \times 10^{-12}$ and $C = 120$ in this case, this estimate of the probable error is $\pm 11.3 \times 10^{-7}$ in the mean index corresponding to any pair of temperature–wave-length coordinates. Obviously, if the estimates in table 10 are reliable and if the 133 residuals of these experiments constitute a representative set, the difference between these estimates of the probable error is an indication that errors other than those listed in table 9 are almost equally important.

[37] Even temperature errors are seen to be of comparatively little importance and, for a substance having such a low dispersion as water, any existing uncertainties in wave length are negligible. These conditions, fortunately, permitted least-squares adjustments on the index, while considering temperatures and wave lengths as exact.

The results of analyses of the residuals, and of their distribution with respect to temperature and wave length, are recorded in figures 17 and 18, respectively. These exhibits confirm the existence of slight systematic errors but indicate, also, that their residual magnitudes cannot materially exceed the accidental errors which have already been established as approximately $\pm 7 \times 10^{-7}$. In figure 18, the apparent superiority of the isothermally adjusted system over the general 13-constant surface, especially at the ends of the spectral interval, is a matter of doubtful merit and is probably a result of the large number of constants (36) involved in the isothermally adjusted system.

In examining the residuals with respect to time, it is not possible to eliminate satisfactorily the systematic effects of temperature by averaging; because, at best, the index was measured at only a very few temperatures during any moderate length of time. However, eight more or less distinct groups of experiments have been recognized, and certain data on the time variation in index measurements are listed in table 11. Here, again, the presence of systematic error is evident, especially in groups 6, 7, and 8 for the temperatures 50, 5, and 55° C, respectively. For the temperature 50° C, work was done not only in group 6 with plus residuals but also in group 2 where minus residuals predominate. Similarly, observations at 5° were made in the unlike groups 7 and 4. Also, it may be added, group 2 includes average negative residuals for 60° C observations, while in group 3 the residuals for the same temperature are predominately positive. Consequently, it appears that there are residual systematic errors, possibly $\pm 1 \times 10^{-6}$, that are not functions of the temperatures used for the observations.

One possible source of some of this error is a slowly variable torsion of the spectrometer cone. Certainly, variable friction is noticed at different room temperatures, and some readjustments of the weight distribution on the bearing surfaces are required and made at different seasons of the year. Small progressive (secular) changes with time during frequent use of such an instrument do not seem impossible.

TABLE 11.—*Refractive-index residuals averaged for certain chronological groupings*

Group number	Number of water samples	Observational time interval	Observational temperatures (centigrade)	Observed points on index surface	Number of residuals		Averaged $10^6 \times (n_o - n_a)$
					+	−	
1	16	May 11 to June 5, 1931	20, 30, 25, 35	16	10	6	+0.2
2	18	July 13 to Aug. 12, 1931	40, 45, 50, 55, 60	25	7	18	−.7
3	15	Sept. 30 to Oct. 27, 1931	40, 60, 20	22	15	7	+.9
4	16	Feb. 23 to Mar. 16, 1932	15, 10, 5, 0	25	6	19	−.9
5	11	Mar. 2 to Mar. 18, 1933	30, 10	18	8	10	−.2
6	6	June 13 to July 10, 1933	50	9	8	1	+1.6
7	5	Jan. 30 to Feb. 6, 1934	5	9	8	1	+1.0
8	6	May 28 to June 18, 1934	55	9	0	9	−1.6

When table 11 is considered in connection with figure 17, it is then evident that the negative residuals at 55° C, most of them in the decidedly negative group 8 and the others in the moderately negative group 2, are not necessarily so significant as appears from figure 17 alone. Indeed, as far as internal evidence is a criterion,[38] it is con-

[38] See, however, discussions in subsections 3 and 4 of section VI.

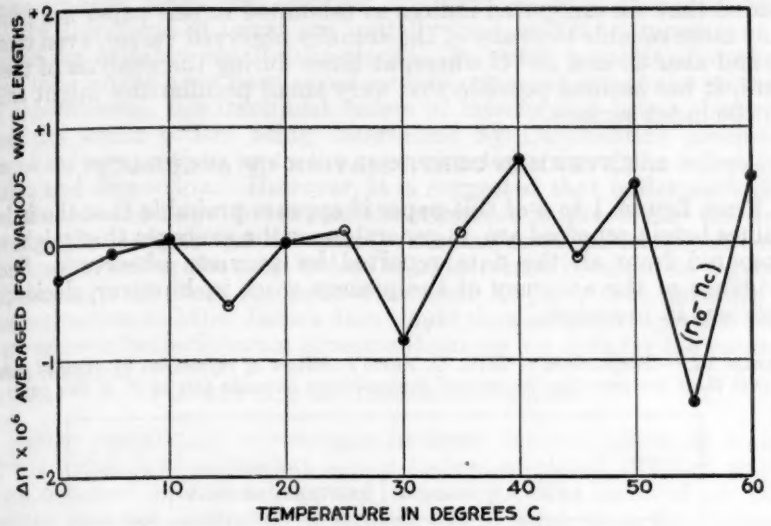

FIGURE 17.—*Temperature distribution of refractive-index residuals,* $\Delta n = (n_o - n_c)$.

Circles show averages for 4 wave lengths; circular dots represent averages for 13 wave lengths. This exhibit indicates that (with possible exception of data at 30 and 55° C) the temperature function used in the computations is suitable for the purpose and that the approved observations are satisfactorily free from systematic temperature errors and their effects. A similar comparison of observed and isothermally adjusted indices would be almost identical with lines directly connecting the circular dots in this figure.

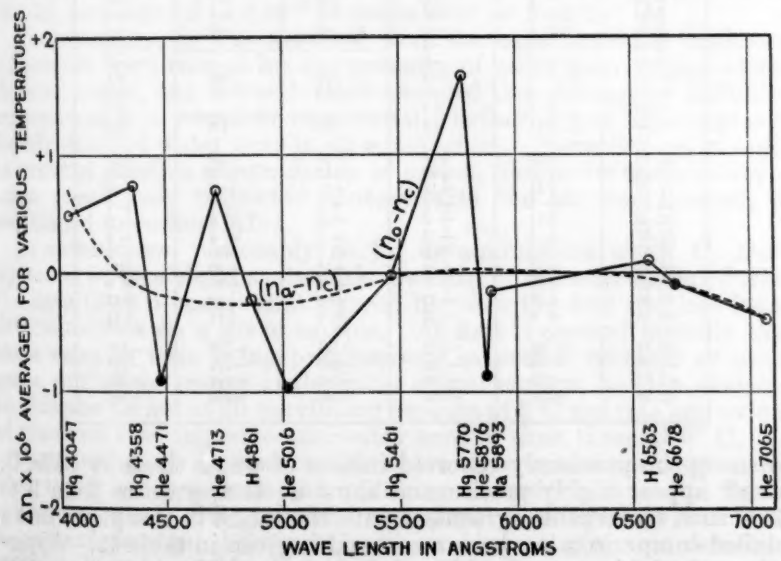

FIGURE 18.—*Wave-length distribution of refractive-index residuals,* $\Delta n = (n_o - n_e)$.

Circles show averages for 9 temperatures; circular dots represent averages for 13 temperatures. This exhibit indicates that systematic errors in using these spectral lines are small and, with possible exception of Hg 5770 A, probably insignificant in sixth-decimal-place refractometry. A similar comparison of observed, n_a, and isothermally adjusted, n_e, indices closely resembles the full broken line, but there is a slightly systematic difference that is quantitatively shown by comparing the dotted curve for $(n_a - n_e)$ with the line $\Delta n = 0$.

cluded that the computed indices as tabulated in this paper are probably more reliable than any of the actually observed values, even those at and near 30 and 55° C where, at times during the analysis of these data, it has seemed possible that very small peculiarities might exist on the index surface.

2. EXTERNAL CONFIRMATION OF ACCURACY

From figures 1 to 5 of this paper it appears probable that the index values herein reported are, in general, near the averages that might be prepared from all the data reported by previous observers. Such evidence of the accuracy of the present work is, however, decidedly deficient in precision.

TABLE 12.—*Comparison of Mlle. O. Jasse's indices of refraction of distilled water with those computed by the general interpolation formula (see eq 3) of this paper*

t°C	Values of $(n_J - n_{NBS}) \times 10^5$				Average
	λ=4358 A	λ=5461 A	λ=5770 A	λ=5791 A	
0.00		+3			+3
.03	+4	+1	+3	+1	+3
3.85	+1	−1	+2	0	0
5.71	+1	+1			+1
5.76	−2	−5	−1	−1	−2
6.55	−1	0	0	0	0
6.63	−3	−3			−3
7.88	−3	−4			−4
8.09	+2				+2
8.52	−4	−5	−7	−7	−6
8.85	−2	−1	0	−4	−2
9.15	−4	−6	−8	−9	−7
9.44	−1	−5			−3
9.65	−5	−8			−6
14.06	−1	−2	+2	+3	+1
15.00	−2	−1	−2	−1	−1
15.24	+6	+4			+5
15.96	+14	+1	+4	+4	+6
21.44	+22	+19	+21	+23	+21
22.19	+9	+10	+12	+9	+10
23.20	+11	+11	+11	+9	+10
23.31	+8	+7	+8	+7	+7
24.42	+11	+7	+10	+9	+9
24.87	+5	+2	+5	+4	+4
27.67	+11	+8	+7	+10	+9
28.16	+31	+14	+11	+20	+19
28.60	+10	+8	+8	+10	+9
28.65	+25	+12	+8	+17	+16
29.25	+9	+13	+9	+13	+11
39.51	−91	−122	−137	−125	−120
41.34	−96	−122	−133	−122	−118
47.45	−110	−138	−150	−140	−134
52.04	−117	−143	−146	−140	−136

Among the previously reported indices of water those by Mlle. O. Jasse[39] appear highly precise and show at temperatures from 0 to 16° C such remarkable agreement with the tables in this paper that a detailed comparison has been made and is given in table 12. Apparently eq 3 of this paper fits Mlle. Jasse's data within this temperature range about as well as if the constants had been determined from her data. This confirmatory evidence of the attainment of accuracy is, of course, not completely satisfactory because of disagreements at higher temperatures. Mlle. Jasse's method permits index determina-

[39] Compt. rend. 198, 163 (1934).

tions without previously assumed approximate data, provided sufficiently thin films of liquid are initially used and the temperature is varied in suitably small increments. It seems possible, however, that time might have been saved by using to some extent the method of coincidences, the fractional orders of interference being observed and the whole orders being determined by Diophantine processes based on assumptions as to the approximate values of the refractive index and dispersion. However, it is suggested that under such circumstances the large errors and uncertainties in previously existing data might lead, almost necessarily in some cases, to erroneous conclusions regarding the total orders of interference involved in a given experiment. If these methods were used in part, then possibly a reexamination of Mlle. Jasse's data would show some changes and perhaps an even better internal agreement among her data for the various wave lengths.

3. EFFECT OF DISSOLVED GASES

During preliminary experiments in index determinations on water it was found that somewhat higher indices of stored distilled water were obtained after heating and degassing. The amount of this increase was not accurately measured but in some cases the increase at room temperatures exceeded 5×10^{-6}. On the other hand, from published data[40] it appears that the density of air-free water does not exceed that of air-saturated water by more than 3×10^{-6} even at 5 to 8° C. This density difference decreases at higher temperatures and is approximately negligible at 30° C. If the relation $(n-1)/d=C$ be assumed, then $\Delta n=\Delta d/3$ and consequently the effect of dissolved air should not exceed 1×10^{-6} in index even at 5 or 10° C.

Consequently, it was assumed that the experimentally indicated differences were caused by the presence of other gases in the stored distilled water, and it was further assumed that during the definitive measurements it would be immaterial whether or not the samples of freshly distilled water were in air equilibrium. Nevertheless, in order to prevent possible accumulation of carbon dioxide or the solution of other gases, only restricted contact with the air was allowed, as mentioned in section III–1.

In some cases, noticeably so for determinations at 0° C, there appeared to be a slight systematic lowering of refractive index during the time (2 to 5 hours) that elapsed between the first and last index determinations on a given sample. At first it seemed possible that these samples were being progressively saturated with air or other gases, during the course of the index measurements, but the evidence on this point is not at all convincing because at 5°C the rate and extent of observed lowering were noticeably smaller than those at 0° C.

Considering all days on which index determinations were made, observer B had predominated in taking the prior sets and A in the subsequent sets of data taken on each day. Consequently, assuming a constant personal difference in the making of minimum deviation settings, it was possible, by simple simultaneous equations, to solve for this personal difference in index, (n_B-n_A), and also for an average value of the time difference, $(n_{\text{prior}}-n_{\text{subseq.}})$. For this purpose the data were considered in two groups, one for temperatures 0 to 20° C,

[40] P. Chappuis, Travaux et Mémoires du Bureau International des Poids et Mesures **14**, D63 (1910).

inclusive, and the other from 25 to 60° C. The results are $+9\times10^{-7}$ for the personal difference, $+6\times10^{-7}$ for the time difference at lower temperatures, and -5×10^{-7} for the time difference at higher temperatures. Moreover, a few data were taken by observer *A* alone at 5° and at 40° C and thus independent estimates of $+1$ and -6×10^{-7} were obtained for the time differences, $(n_{\text{prior}}-n_{\text{subseq.}})$, at these respective temperatures. This confirmation of the time differences is as good as should be expected considering the possibility of very slight changes in the effective prism angle from hour to hour, or rather the differences between the actually existing angle and the linearly interpolated values that (see section III–3) were obtained from the initial and final angle measurements on a given day.

Possibly, then, during these measurements the index of water progressively decreased slightly while the water was held at temperatures below room temperature and increased slightly while it was held above room temperature. The increase at higher temperatures is, of course, in accord with expectations regarding possible dissolved glass or metal, but in both cases the changes are in the seventh decimal place and opposite in sign to expectations that might be based on temperature-error effects as temperature equilibrium is slowly approached.

4. STRUCTURE OF WATER

In order to explain the maximum density of water at 4° C, the minimum molecular heat near 35°, minimum compressibility near 40°, and certain other known facts regarding the properties and behavior of water, it has often been assumed that liquid water consists of a mixture of polymers, say of tri-, di-, and monohydrols, coexisting in reversible equilibrium.[41] Study of X-ray patterns and of Raman spectra has pointed however, to the abandonment of such simple ideas as to the nature of association in water (and in many other liquids). The hydrols hypothesis was superseded by the molecular group conception or cybotactic condition according to which temperature greatly influences distances, orientations, molecular forces, and other factors affecting the size and internal regularity of relatively large groups having ill-defined boundaries. More recently, liquid water has been qualitatively pictured in terms of coordination theory as a "broken-down ice structure" with coordination persisting in definite degree dependent chiefly on temperature.[42]

During these measurements on the refractive index of water the authors have been mindful of the possibility of detecting slight peculiarities in index that might be directly attributed to relatively sudden changes in the degree of association or in other characteristics of the water molecules. In this connection, it may be mentioned that the apparent minima in values of l^2, as shown in figure 10, and the corresponding negative residuals in index, figure 17, occur at temperatures 30 and 55° C, which are near those at which Wills and Boeker[43]

[41] See, for example, W. D. Bancroft and L. P. Gould, J. Phys. Chem. **38**, 197–211 (1934); J. Duclaux, J. chim. phys. **10**, 73–109 (1912).

[42] See, for example, G. W. Stewart, Phys. Rev. [2] **37**, 9–16 (1931); J. D. Bernal and R. H. Fowler, J. Chem. Phys. **1**, 515–548 (1933); Michel Magat, Ann. phys. **6**, 156 (1936); Paul C. Cross, John Burnham, and Philip A. Leighton, J. Am. Chem. Soc. **59**, 1134 (1937).

[43] A. P. Wills and G. F. Boeker. Phys. Rev. [2] **46**, 908 (1934). Elementary considerations indicate that, for diamagnetic substances, the index should decrease slightly if specific susceptibility increases in absolute value without a compensating decrease in density. In this connection, however, Samuel Seely, Columbia University, in a private communication to the authors, reports good general agreement with the results by Wills and Boeker, but much more regular data with no humps. He finds a marked change in slope at or near 45° C. See Phys. Rev. [2] **53**, 662 (1937).

found humps on their curve of the specific magnetic susceptibility of water. Also, the shape of the curve for k in figure 10 may, perhaps, correspond with the sudden disappearance of the Raman band, $\Delta\nu$=500 to 700 cm^{-1} when t rises above 37°, as reported by Magat;[44] or it may correspond with the change in temperature rate at which certain absorption maxima in the near infrared are shifted toward shorter wave lengths, as found by Ganz[45] near 40° C.

It has been generally assumed that equilibrium between the temperature and the degree of association, or coordination, is very quickly established, and a confirmatory report was issued by La Mer and Miller[46] who, by an interference method with a precision of $\pm 3\times10^{-6}$ investigated the index of water (at 20° C only) as a function of time. Nevertheless, the authors must state that at times during their experiments it has seemed that complete equilibrium is difficult to obtain. The average trend toward lower index as time elapsed during measurements at 0° C, as mentioned in the preceding section, was scarcely large enough to seem decisive but on several occasions water was allowed to remain in the prism overnight or longer and the subsequent measurements yielded abnormal values of index that are not easily explained. Temperature uncertainty in its direct effect on index is a negligible factor at low temperatures where these abnormalities were especially noticed. There are, however, other factors that may require time for equilibrium. Dissolved metal or glass would increase the index but in a number of instances the measured index decreased after one or two days. Dissolved air or gases might decrease the index slightly, but these samples of 9 ml were in contact with only 1 ml of air. In fact, the magnitudes and algebraic signs of these changes with time are such that they are not at present satisfactorily explained.

A concise record of these auxiliary experiments and of the systematic nature of the abnormal changes in index is given in figure 19 where they are plotted against the temperature at which the measurements were made. All of these indices, determined after considerable lapse in time, were compared with indices as computed by the general formula (see eq 3) of this paper, and the differences (n_o-n_c), were averaged for several wave lengths and then plotted for comparison with each other and with the strictly normal condition $(n_o-n_c)=0$. Curve A appears to be characteristic of water that has remained in the prism for about 28 hours. Curves C and D are similar but represent data taken after from 1 to 3 days and the indices may be slightly high because of possible contamination with beeswax, which in these auxiliary experiments was used in cementing the prism windows. Curve B, however, should be altogether different because it represents data on water distilled in vacuo and sealed in the special vacuum-type prism *III* in contact with water vapor only. From published data it appears that a value of -14×10^{-6} is to be expected for (n_o-n_c) in this case, but curve B is found below curve A by something less than one-half that amount. This may mean that the windows or the Duco cement yielded and allowed partial atmospheric pressure on the water; or possibly the Duco proved considerably more soluble than the

[44] M. Magat. J. phys. et radium [7] **6**, 179 (1935). See, however, G. Bolla. Nuovo cimento **12**, 243 (1935), who reports that certain bands at 510 and 780 cm^{-1} are present at 42° C.
[45] Ernest Ganz. Ann. Physik [5] **26**, 331-348 (1936).
[46] Victor K. La Mer and M. L. Miller. Phys. Rev. [2] **43**, 207 (1933).

beeswax that was used when the data of curves *C* and *D* were taken. In its slope, however, curve *B* closely parallels curves *A*, *C*, and *D*.

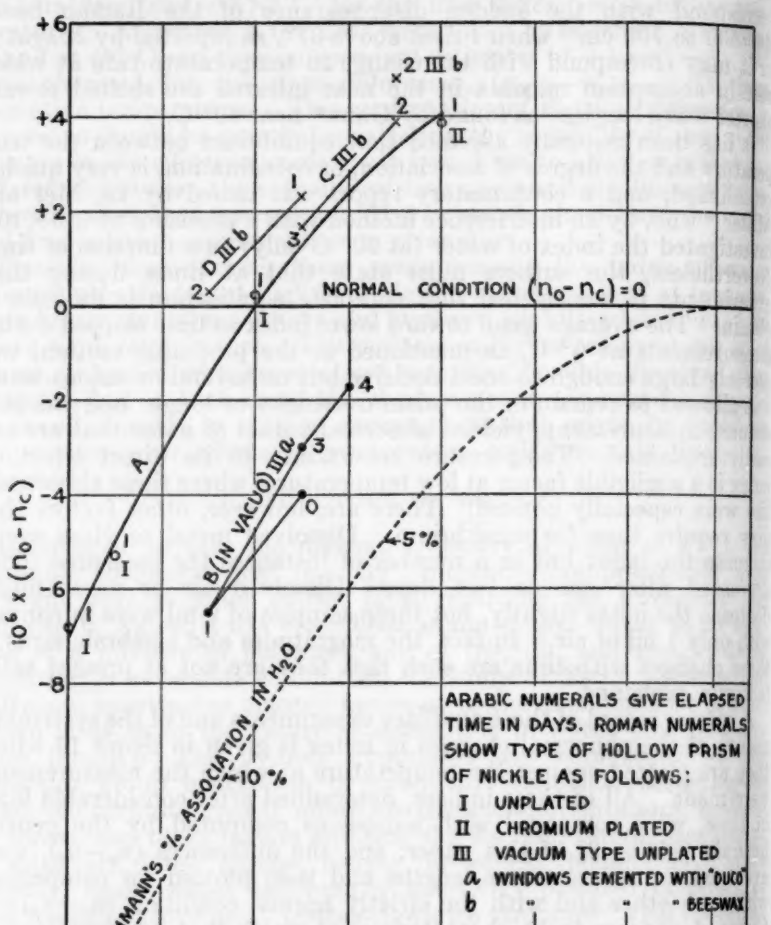

FIGURE 19.—*Abnormal index of refraction of distilled water after prolonged contact with glass and nickel.*

All points represent averages for several wave lengths, and observed indices, n_o, are compared with indices, n_c, computed by the general interpolation formula (see eq 3). Circles (curve *A*) indicate measurements with regular approved sampling and procedures but after the samples had remained 1 day in the prism. Dots (curve *B*) indicate values for a sample of water distilled and measured in vacuo but perhaps contaminated with Duco cement. Crosses (curves *C* and *D*) indicate measurements at atmospheric pressure on a second and a third sample, after distillation in vacuo, but perhaps there is slight contamination with beeswax.

In considering figure 19 the important matter is this slope of the curves with respect to the normal condition. It should be noted that

the progressive changes that occurred from 0th to 1st day on curve *B*, from 2d to 3d day on curve *C*, and from 1st to 2d day on curve *D* are decreases and therefore can not be directly ascribed to progressive contamination as such. Moreover, curve *A* crosses the axis near 20° C at which temperature La Mer and Miller made their tests and likewise found no change in index as a function of time.

As a possible partial explanation of these data it is suggested that refractivity is increased by the solution of glass and metal, and also simultaneously decreased by some structural change that is proportional in amount to the existing degree of thermally variable association, coordination, or "ice molecule" content.[47] From figure 19 it is possible to estimate that at 70° C, above which rate of change in the ice-molecule content is probably small, the direct effect of solution would be approximately $+7\times10^{-6}$ in index after 28 hours, but that the effect of solution does not increase proportionately during a second or third interval of like duration. The accompanying decrease in index is, apparently, of the order of 1×10^{-6} for each percent of ice-molecule content as estimated by Tammann.

These suggestions based on the auxiliary experiments with long enduring contact between water and prism are, also, probably applicable to the results found by the direct analysis of definitive data in the preceding section (VI–3), and thus it may be inferred that contamination was not entirely absent in the definitive refractive-index measurements made with normal procedures. It is, however, untenable to assume that any sizable index changes similar to those illustrated in figure 19 could have occurred in the normal procedure, because the said direct analysis of definitive data shows that the average differences between prior and subsequent sets of observations taken on a given day are entirely matters of the seventh decimal place of index.

Interest in all of these auxiliary results is, therefore, almost entirely academic. The interesting difficulty is to account for the lower indices at low temperatures. A slight decrease in coordination proportional to the initially existing degree of coordination might conceivably be occasioned by progressive solution and possible ionization. Such a change in coordination, however, is supposed to permit closer packing of the water molecules and hence the algebraic signs conflict with such a conception. Fortunately, there is one clearly established and satisfactory aspect of all indications of systematic error in these experiments. It is the apparent smallness of the resultant effects on the approved indices of refraction of water as tabulated in this paper. There is no indication of accidental or systematic error in excess of ±1 or 2×10^{-6}.

The authors acknowledge indebtedness to numerous members of the Bureau's Staff for valued suggestions, advice, and assistance throughout this work.

WASHINGTON, January 18, 1938.

[47] See, for example, G. Tammann, Z. anorg. allgem. Chem. **158**, 4 (1926). Possibly, however, Tammann's percentages should be considered simply as changes in association rather than as estimates of the total extent thereof.

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CROSS-CONNECTIONS IN PLUMBING SYSTEMS

By Roy B. Hunter, Gene E. Golden, and Herbert N. Eaton

ABSTRACT

This paper deals principally with the technical aspects of the problem of preventing the backflow of water from plumbing fixtures into water-supply systems. It starts with a general review of the subject, including a brief history of previous work on the subject, a classification of cross-connections, and a brief discussion of vacua and siphon action. This is followed by a mathematical and experimental analysis of the conditions tending to produce backflow into a supply line. This analysis makes it possible to determine the worst conditions, as regards backflow, that can occur in any building supply system, and to determine minimum requirements for the positive prevention of backflow under these conditions. Specifically, the minimum pressure that can occur in any system, the maximum rate at which water can be removed from the supply risers under this minimum pressure, the smallest air gap between a faucet and plumbing fixture that can be safely allowed under the worst conditions, and the essential performance characteristics of a siphon-breaker are determined. The effectiveness of various types of siphon-breakers in preventing backflow is discussed, and the operation of one type of flush valve is explained in order to show the essentials of a stable flush valve, that is, one which will not open under any possible reduction in supply pressure. Finally, there is given a brief review of the entire subject of preventing backflow from plumbing fixtures, in which two distinct methods of attack are pointed out, and the merits of each are discussed. The conclusions relate only to the technical aspects of the subject and do not take the form of proposed health or plumbing regulations.

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I. INTRODUCTION

1. EARLY ATTENTION TO CROSS-CONNECTIONS

For several decades, cross-connections and their menace to health have been subjects of active interest to engineering, public health, and trade organizations, but as yet no generally satisfactory conclusions, either as to the extent to which cross-connections may be a menace to health or as to practical regulatory measures for controlling this condition, have been reached. The subject was presented to the New England Water Works Association as early as 1894 [1]* and was later made the subject of committee investigations and reports by the New England Water Works Association [2], the American Water Works Association [3], and the American Society of Sanitary Engineering [4]. The subject has also been frequently before the American Public Health Association [5], the National Association of Master Plumbers [6], and other national, sectional, and local organizations for discussion and official action. A large number of papers on the subject have been published in engineering, public health, medical, and trade journals. For the most part, publications on the subject deal with the occurrence of cross-connections and their menace to health rather than with a practical correction of the situation.

Numerous epidemics have been traced or attributed to cross-connections in plumbing systems [7]. Probably the most publicized and most thoroughly investigated case on record was that of an outbreak of amoebic dysentery in a hotel during the World's Fair in Chicago in 1933 [8]. Lists of epidemic outbreaks attributed to cross-connections in plumbing systems have been compiled, but relatively few of the available records give detailed information, either regarding the cross-connections to which the epidemic was attributed or the means by which it was determined that the epidemic was caused by the cross-connection.

Among the published information dealing more directly with the correction or removal of the hazards of cross-connections in plumbing systems, the reports of investigations at the University of Wisconsin under the direction of Professor F. M. Dawson [9], and at the Massachusetts Institute of Technology under the direction of Professor T. R. Camp [10] are of particular interest. Two more recent papers by Professor Dawson and Mr. Kalinske continue with the analysis of the problem [11, 12]. A number of reports of investigations in Germany [13 to 19] on the problem of cross-connections have been published. None of these papers contains a complete analysis of the problem in respect to (1) a classification of cross-connections into physical types; (2) a determination of the limiting conditions in water-supply systems as they affect backflow through a cross-connection; and (3) a determination of the minimum requirements for the prevention of backflow through a cross-connection of a given type.

2. PURPOSE AND SCOPE OF THE INVESTIGATION

In February 1936, the National Bureau of Standards commenced an investigation of cross-connections in plumbing systems for the purpose of obtaining the technical information and data required for

*Numbers in brackets indicate literature references at the end of this paper.

the determination of minimum requirements for preventing backflow of water into the water-supply lines from plumbing fixtures or drains and for putting this information into a form available for the use of Federal, State, and municipal authorities in the formulation of effective health regulations applying to plumbing.

The investigation as planned included: (1) A survey of the literature on the subject, with the collection and analysis of available data; (2) the definition and classification of cross-connections; (3) an analysis of the physical conditions and principles involved; (4) experimental verification of the analysis; and (5) correlation of data for practical application in eliminating the hazards of cross-connections.

The ultimate purpose of the investigation is to establish an organized body of information on this subject that will afford a basis for decreasing, or even eliminating entirely, the hazards due to cross-connections. Since the accomplishment of this purpose is dependent on the cooperative endeavors of a number of agencies and interests—governmental, engineering, construction, and owners or operators—no complete and satisfactory solution of the problem of cross-connections by a single agency or individual can be expected. However, a common ground or basis of agreement must be found, and this paper is offered as a contribution to that end, rather than as a complete solution from the standpoint of health regulations.

In fact, the paper should be looked upon as a progress report, rather than as a complete and final report on the investigation. It will be some time before all phases and details of the project as it is now conceived will be finished; and since the theoretical analyses and experimental verifications of certain aspects of the problem have been completed, it seemed advisable to publish these data and analyses without delay, so that they would thus be made conveniently available to other investigators and to those who may wish to make practical application of the results.

II. OUTLINE OF THE PROBLEM

1. DEFINITION AND CLASSIFICATION OF CROSS-CONNECTIONS

A cross-connection may be defined as any physical connection or arrangement of pipes between two water piping systems whereby water may flow from one system to the other, the direction of flow depending on the direction of the pressure differential between the two systems. A cross-connection becomes a hazard to health when one system carries a water used for human consumption and the other carries an impure or contaminated water. It will be convenient for purposes of discussion and analysis to divide cross-connections into two general classes, *direct* and *indirect*, although there is no sharp demarcation between the two in principle.

A *direct cross-connection* may be defined as a continuous inclosed interconnection between two piping systems, such that the flow of water from one system to the other may occur whenever a pressure differential is set up in the connection between the two systems. Examples: Interconnections between dual water-distributing systems, completely submerged inlets from water-supply lines to closed plumbing fixtures, tanks and vats, continuous water connections between the supply and drain systems, priming lines to pumps, etc.

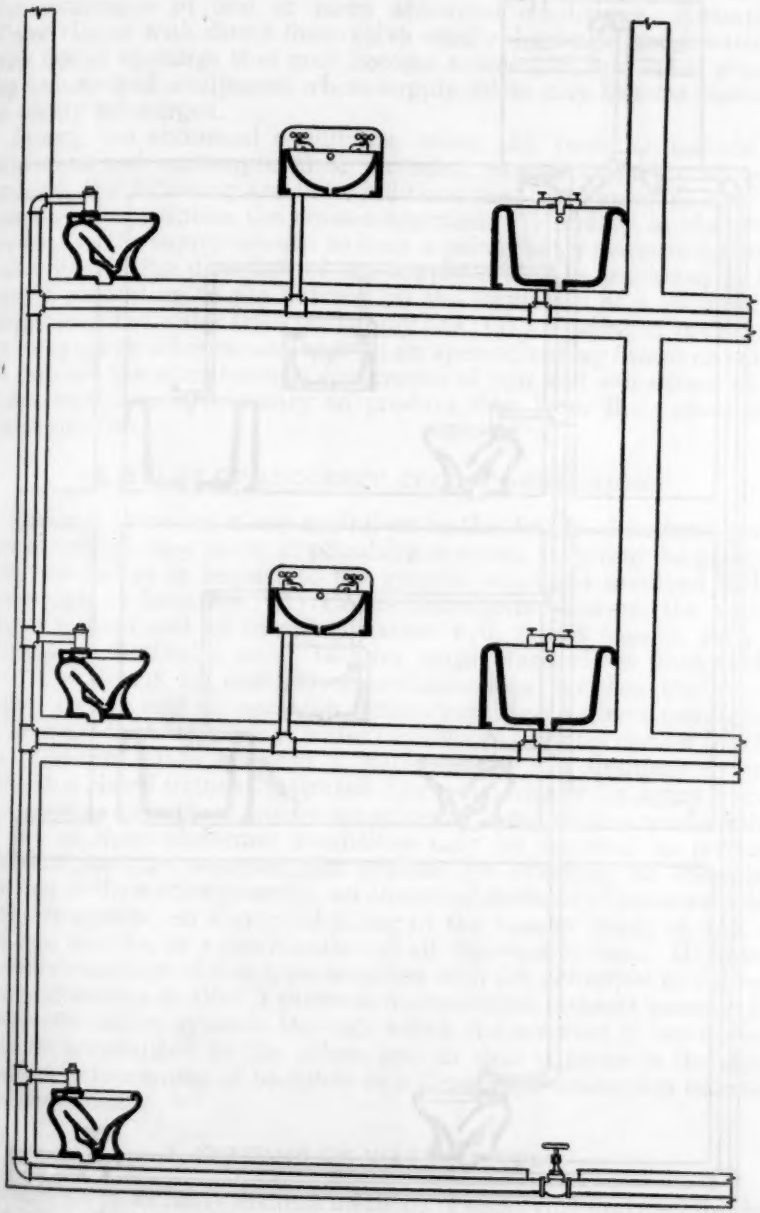

FIGURE 1.—*Up-feed supply system.*

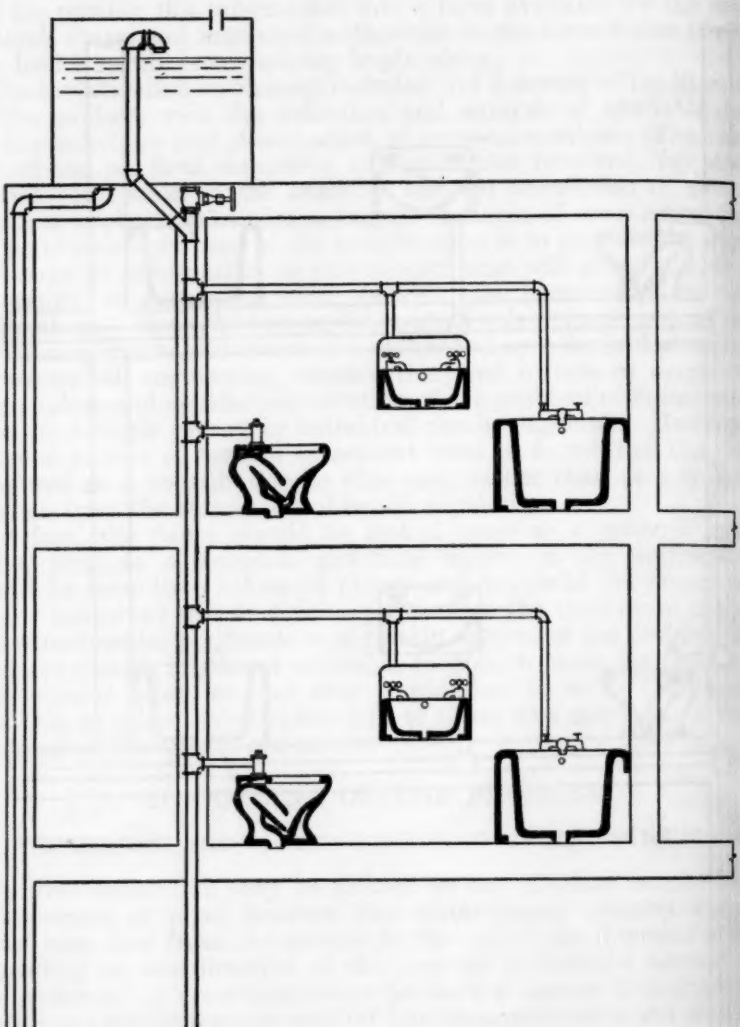

FIGURE 2.—*Down-feed supply system.*

An *indirect cross-connection*, frequently referred to as a potential cross-connection, is one in which the interconnection is not continuously inclosed, and the completion of the cross-connection depends on the occurrence of one or more abnormal conditions. Examples: Water closets with direct flush-valve supply, bathtubs and lavatories with faucet openings that may become submerged, and other plumbing fixtures and equipment whose supply inlets may become partially or wholly submerged.

Among the abnormal conditions, using the term to include all conditions not contemplated or intended, as well as in the sense of unusual, the following are the conditions that may occur or may be necessary to complete the cross-connection: (1) A drop in the static pressure in the supply system to such a point that a pressure differential acting in the direction of the supply system is produced in the supply connection to the fixture; (2) the formation of a vacuum by displacement of water from the supply line; (3) a flooding of the fixture by stoppage or other causes; and (4) an open or leaking faucet or valve. In general, the simultaneous occurrence of two and sometimes all of these conditions is necessary to produce flow from the fixture into the supply line.

2. TYPES OF INDIRECT CROSS-CONNECTIONS

Although there are many variations in the details of indirect cross-connections as they occur in plumbing systems, they may be grouped into two classes in respect to the general principles involved in the prevention of backflow: (1) Cross-connections between the water-supply system and an open-top fixture with faucet supply, such as washbasins, bathtubs, sinks, laundry trays, water-closet flush tanks, etc. (figs. 3 and 4); and (2) cross-connections between the water-supply system and an open-top fixture requiring a direct connection for pressure flushing, such as water closets and pedestal urinals (fig. 5).

A cross-connection between a water-supply and drainage system through a closed fixture illustrated diagrammatically by figure 6 may be classed as an indirect cross-connection by some, since a combination of two or more abnormal conditions may be required to produce backflow into the water-supply system; for example, an abnormal decrease in the service pressure, an abnormal increase of pressure in the drainage system, an abnormal filling of the fixture, tank, or vat, as the case may be, or a combination of all these conditions. However, a cross-connection of this type complies with the definition of a direct cross-connection in that it presents a continuous inclosed passage between two piping systems through which the pressure in one system may be transmitted to the other, and in that it presents the same problem in prevention of backflow as a direct pipe connection between the two systems.

3. SYSTEMS OF WATER SUPPLY

There are three fairly distinct methods of supplying and distributing water in buildings: (1) The up-feed system with a direct service pipe to a service main (fig. 1); (2) the down-feed system from an overhead tank exposed to atmospheric pressure (fig. 2); and (3) the pressure-tank supply with either up-feed or down-feed distribution, the tank pressure being maintained either by a direct connection with a pressure

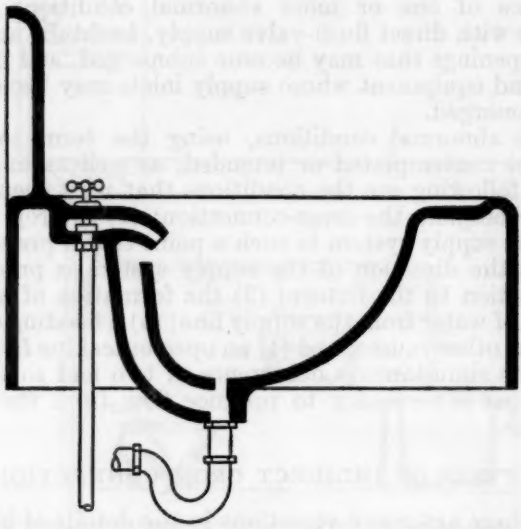

FIGURE 3.—*Indirect cross-connection between open-top fixture and faucet supply.*

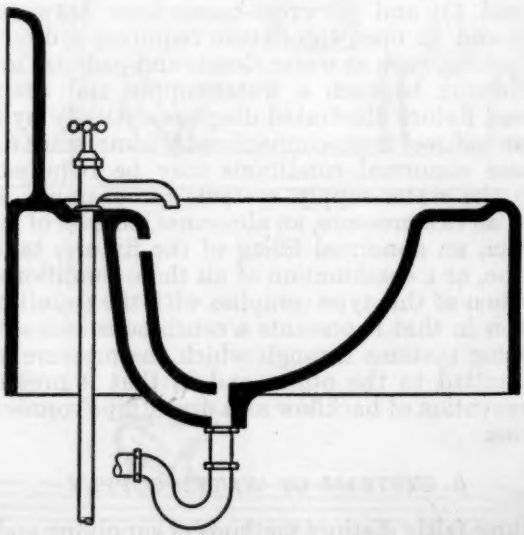

FIGURE 4.—*Indirect cross-connection between open-top fixture and faucet supply.*

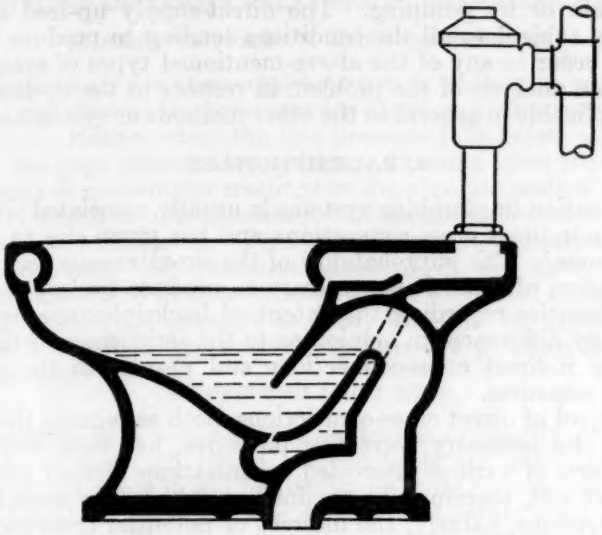

FIGURE 5.—*Water closet with direct connection for pressure flushing.*

Indirect connection.

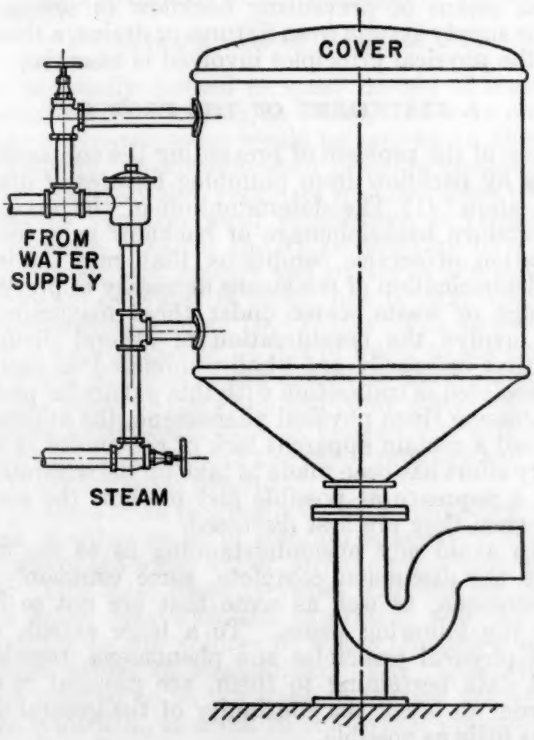

FIGURE 6.—*Direct cross-connection through a closed fixture.*

supply main or by pumping. The direct-supply up-feed system is potentially subject to all the conditions tending to produce backflow that may occur in any of the above-mentioned types of systems, and therefore an analysis of the problem in respect to the up-feed system will be applicable in general to the other methods or systems of supply.

4. BACKSIPHONAGE

Siphon action in plumbing systems is usually associated with backflow in the indirect cross-connections and has given rise to the term *backsiphonage*.[1] The improbability of the simultaneous occurrence of a combination of conditions necessary to produce backsiphonage and the uncertainties regarding the extent of backsiphonage have given rise to many differences in opinion as to the seriousness of the hazard created by indirect cross-connections and also as to the necessary corrective measures.

The subject of direct cross-connections, both as regards their prevalence and the necessary corrective measures, has been well covered in the reports of various interested organizations already referred to. This report will, therefore, be confined mainly to the second class of cross-connections, namely, the indirect or potential cross-connections between the water supply and the drainage system through plumbing fixtures and other mechanical equipment.

Since the final purpose of the investigation is to indicate an effective and practical means of preventing backflow of sewage and waste water into the supply system from fixtures or drains, a thorough understanding of the physical principles involved is essential.

5. STATEMENT OF THE PROBLEM

The solution of the problem of preventing the contamination of the water supply by backflow from plumbing fixtures or drains involves two distinct steps: (1) The determination of the maximum effects tending to produce backsiphonage or backflow as a consequence of any combination of service conditions that may be encountered; and (2) the determination of the means necessary to prevent the backflow of sewage or waste water under these maximum conditions. Both steps involve the consideration of several distinct physical phenomena that ordinarily are wholly unrelated to each other, but which are associated in connection with this particular problem. As a result, in discussing these physical phenomena, the authors have been unable to avoid a certain apparent lack of continuity in the development. Every effort has been made to take up the separate phenomena in as logical a sequence as possible and to show the connection between them when they are first discussed.

In order to avoid any misunderstanding as to the use of terms and to make the discussion complete, some commonly understood physical phenomena, as well as some that are not so familiar, are discussed in the following pages. To a large extent, the detailed discussion of physical principles and phenomena, together with the experimental data pertaining to them, are grouped in sections III and IV in order to break the continuity of the general discussion of the subject as little as possible.

[1] The corresponding term, *Rücksaugung*, has come into common use in Germany.

6. DEFINITIONS OF TERMS RELATING TO PRESSURES AND VACUA

(a) ABSOLUTE PRESSURE AND GAGE PRESSURE

The pressure in a water-supply system is ordinarily expressed as *gage pressure;* that is, the pressures are based on atmospheric pressure as a datum. Hence, when the line pressure falls below atmospheric pressure, the gage pressure is negative. In some cases it is desirable to refer gage or manometer readings to the absolute scale of pressures, the zero of which is approximately 14.7 lb/in.^{2} below normal atmospheric pressure at sea level. Pressures that are so measured are called *absolute pressures.* All pressures involved in the analysis of the phenomena discussed in what follows will be expressed in this scale of pressures. If a gage pressure is used, this will be expressed as a difference between the corresponding absolute pressure and atmospheric pressure.

(b) PRESSURE UNITS USED

The pressure in a water-supply system is ordinarily expressed in pounds per square inch (when English units are used), but for the purposes of this paper it will frequently be more convenient to express it as the height in feet of a water column that would exert at its base a pressure equal to the given pressure in pounds per square inch.

Atmospheric pressures are commonly expressed in inches height of a column of mercury, but obviously they may be expressed equally well in pounds per square inch or in feet height of water column.

(c) DEFINITION OF A VACUUM

A vacuum is usually defined as space devoid of matter. This is the hypothetical perfect vacuum, in which, if it were obtainable, the pressure in the evacuated space would be zero on an absolute scale of pressures. Actually, an absolute-zero pressure cannot be produced over water, since some water vaporizes into the space over the water and continues to vaporize until equilibrium is established. This equilibrium pressure is called the vapor pressure of water, and its value depends on the temperature and purity of the water. At 0° C the vapor pressure of water is small, but it increases rapidly with increase in temperature, and at 100° C it is equal to standard atmospheric pressure, approximately 34 feet of water at sea level.

Similarly, if the water contains dissolved air or other gases, as is usually the case, some of the gases will come out of solution into the evacuated space until equilibrium is established, and each gas will exert a pressure independently of the vapor pressure and of the partial pressures of the other gases present.

The total pressure in an inclosed vacuum in equilibrium with water containing air or other gases in solution is equal to the sum of the partial pressures of the water vapor, air, and other gases at the existing temperature. This total pressure varies with the temperature, and, for dissolved gases, also with the saturation and the ratio of the evacuated volume to the volume of water remaining in the system when the latter comes to equilibrium. The equilibrium pressure, which will be referred to as the *limiting vacuum pressure* and designated by the symbol h_e, is small in cold-water systems, but in hot-water systems its value may equal or exceed the atmospheric pressure h_a if the temperature equals or exceeds the boiling temperature at atmospheric pressure.

The following definitions will be observed in this paper in referring to vacua in water-supply systems:

A *vacuum* is any space in a water-supply system from which water has been displaced by water vapor, air, or other gases, and in which the pressure is less than the prevailing atmospheric pressure.

A *limiting vacuum* is a vacuum in an inclosed space in which the absolute pressure is equal to the equilibrium pressure h_e.

A *partial vacuum* is any vacuum in which the pressure lies between the prevailing atmospheric pressure h_a and the limiting pressure h_e.

It is to be understood that the values of h_a and h_e depend on many different factors, some of which have been mentioned above. Hence, in general, we cannot assign definite values to these two pressures. However, it will be convenient in the following discussion to regard h_e as having a limiting value of 34 feet, expressed as height of water column, and to regard h_e as representing in general a very low absolute pressure. With this understanding, the symbols h_a and h_e will usually be employed in this paper in the discussion of vacua as if they had definite fixed values.

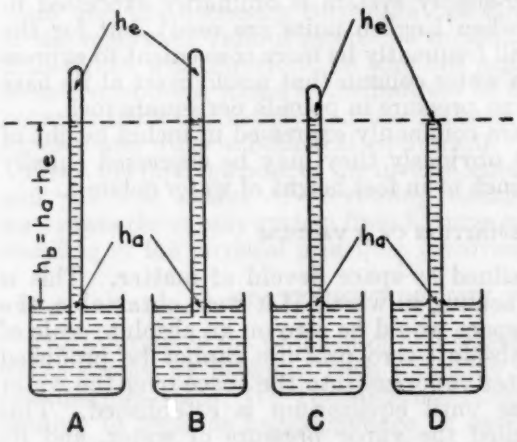

FIGURE 7.—*Simple liquid barometer.*

7. ATMOSPHERIC PRESSURE AND SIPHON ACTION

The part played by the atmospheric pressure in producing siphon action or backflow in plumbing systems apparently has not been understood thoroughly by some who have discussed this subject. Consequently, it seems advisable to state here some of the relations involved in siphon action.

The atmosphere at sea level exerts a pressure of approximately 14.7 lb/in.^{2}, equivalent to the pressure at the base of a column of water 34 feet in height or at the base of a column of mercury 30 inches in height. Therefore, the atmosphere at sea level will support a column of water approximately 34 feet in height in a tube against a perfect vacuum (zero absolute pressure). Actually, at any given time and place, the height of the water column, illustrated by a simple water barometer in figure 7, will be given by the equation $h_b=h_a-h_e$. If there are no dissolved gases in the water, then when the barometer tube is raised and lowered successively, figure 7 (*B*, *C*, and *D*), the evacuated volume over the column of water will increase or decrease correspondingly, and the length of the column of water h_b will be the same in each case, once the system has come to equilibrium. If the water contains air in solution, the system will come to equilibrium with slightly different values of the equilibrium pressure h_e in the cases illustrated, since the change in the relative volumes of vacuum

and water exposed produces a change in the partial pressure due to the dissolved air, as explained in the preceding section. In any case, h_b represents the limit in the height that water can be lifted from an open vessel by siphon action in a completely filled siphon tube, since the atmospheric pressure supplies the entire lifting force. This limit, as defined here, refers to atmospheric pressure at sea level, and it decreases proportionately as the atmospheric pressure decreases with elevation above sea level.

Since the pressure exerted at the base of a liquid column varies directly as its density, the maximum height to which a liquid can be lifted by siphon action varies inversely as the density of the liquid. Therefore, the limit in the height to which a mechanical mixture of air and water, such as may flow into a partially submerged inlet, can be lifted will be approximately equal to $h_b\ (\rho_w/\rho_m)$, where ρ_w is the density of the water, and ρ_m is the density of the mixture, provided the velocity of flow through the siphon is sufficient to prevent the air from separating from the mixture in the siphon tube. If the velocity is too low, the air will separate from the water and collect at the top of the tube (air-lock) and will stop the siphon action. It is impossible to connect this theoretical limit in the height of lift of a mixture of air and water by siphon action numerically with the height of lift in a water-supply system because there is no known means of determining the exact conditions, such as velocity and height of lift, under which air-lock of the siphon will or will not occur. The most that can be positively stated in this respect is: If siphonage of a mixture occurs, the limit in lift may be many times the limit of lift for pure water through a completely submerged siphon inlet.

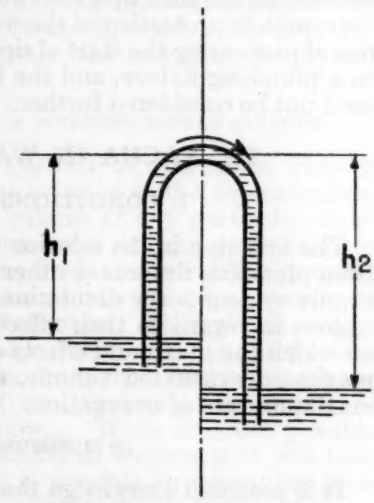

FIGURE 8.—*Simple siphon.*

The quantitative relation of the forces acting to produce siphonage may be demonstrated by reference to the simple siphon, shown in figure 8. Considering the component of pressure acting to produce flow in the direction of the arrow as positive, there will be a component of $+h_a$ acting on the inlet,[2] a component of $-h_a$ acting on the outlet,[3] a component of $-h_1$ produced by the column of water in the inlet leg and a component of $+h_2$ produced by the column in the outlet leg. The resultant pressure will be the sum of the components

$$+h_a-h_a+h_2-h_1=h_2-h_1$$

There is, therefore, a head of h_2-h_1 available to produce flow in the tube, and the velocity at any time will be such that this available head h_2-h_1 is exactly equal to the friction loss in the tube plus the entrance and exit losses.

[2] [3] At the level of the external water surface in each case.

It should be pointed out that the sole functions of the outlet leg are: (1) To reduce the pressure at the top of the siphon tube so that the atmospheric pressure can lift the water in the inlet leg, and (2) to provide a passage for flow. Hence, flow in the inlet leg will take place in exactly the same manner, for a given reduction in pressure at the top of the siphon, regardless of how the reduction in pressure at the top of the siphon is produced. Therefore, the existence of a vacuum, whether it be a partial vacuum or the limiting vacuum, in the water-supply system will produce backflow through a supply branch, as a result of atmospheric pressure acting through the supply branch, in exactly the same manner and with the same limits of lift as would be produced by a complete siphon tube with an outlet leg capable of maintaining the same pressure in the top of the siphon as exists in the vacuum.

If the positive prevention of backflow into any part of the water system, rather than flow into the water mains, is taken as the criterion for complete protection of the water supply, the problem then becomes one of preventing the start of siphon action in any water-supply branch to a plumbing fixture, and the limits of height of lift and rate of flow need not be considered further.

III. VACUA IN WATER-SUPPLY SYSTEMS

1. CONDITIONS TO BE CONSIDERED

The first step in the solution of the problem of preventing backflow from plumbing fixtures or other mechanical equipment into the water-supply system is the determination of the limits applying to the conditions in regard to their effects in producing backflow. The limits on which the maximum effects depend are the minimum pressure, the maximum evacuated volume, and, closely related to the latter, the maximum rate of evacuation.

(a) MINIMUM SERVICE PRESSURE

It is common knowledge that the service pressure in water-supply systems may sometimes fail completely, as by the breaking of a supply main by a shutdown or breakdown of a pumping system, and, so far as a building water-supply system is concerned, may approach complete failure under heavy demands on water mains, as from fire pumps, or from other unusual heavy service demands. Since no one can predict with certainty when or where such failures in the main service pressure will occur, there is only one minimum limit that can be established for service pressures for buildings in general, namely, a drop in service pressure that will reduce the pressure at the base of the building water-supply system to the limiting vacuum pressure over water, h_v.

(b) MINIMUM PRESSURE IN BUILDING SUPPLY SYSTEMS

Since we can set no definite limit for the main supply pressure short of the limiting vacuum pressure, the same limit must apply to an unvented building supply system. However, the minimum limit will be reached more frequently in the building supply system than in a supply main because the former is higher than the latter. The limiting pressure h_v will occur at the top of any unvented up-feed system whenever the service pressure falls to atmospheric pressure at a level 34 feet or more below the top.

(c) MAXIMUM EVACUATED VOLUME IN BUILDING SUPPLY SYSTEMS

Just as occurs in the tube of a water barometer, a vacuum will form in the top of an unvented water-supply system whenever the service pressure from any cause falls to atmospheric pressure at a level 34 feet below the top, and the pressure in the vacuum will be the limiting vacuum pressure h_v. If the system is vented or leaking at the top, a partial vacuum will be formed in which the pressure will lie between the limiting pressure h_v and atmospheric pressure h_a while the service pressure is dropping and will become equal to h_a when the system comes to equilibrium. In either case, whether the system is vented or unvented, the evacuated volume obviously will be exactly equal to the volume of water that has flowed out of the system and may extend to occupy its entire internal volume, depending on a drop in service pressure at the base of the system to h_v in the case of an unvented system, and on a drop to h_a in the case of a vented or leaking system. Therefore, the only definite limit that can be set for the maximum evacuated volume is the internal volume of the system expressed in terms of the diameter and length of the pipe of which the system is constructed.

(d) MAXIMUM RATE OF EVACUATION OF BUILDING SUPPLY SYSTEMS

If the system is vented or leaking, the rate of evacuation (rate of outflow of water) is quite as important a factor in the determination of maximum effects as the evacuated volume at any particular time. The maximum rate of evacuation will have a definite application in determining the capacities of vents required to control the pressure in a supply system within any selected limits found necessary to prevent backflow through its supply branches. The volume rate of evacuation of a supply system will be exactly equal to the volume rate of outflow (displacement) of water from the system and can be computed from the sectional area of the pipe and the velocity of outflow, provided these factors are known. While it is not possible to predict definitely the maximum velocity of outflow that will take place in particular supply systems, it is possible to determine from simple hydraulic principles a maximum limit of velocity in terms of the diameter of the pipe through which the outflow takes place, which limit is unlikely to be reached and will not be exceeded in any system under actual service conditions. These hydraulic principles are given in section IV–1 of this paper in connection with the experimental data pertaining to this phase of the problem.

(e) ASSUMPTIONS RELATIVE TO CONDITIONS IN BUILDING SUPPLY SYSTEMS

Since we cannot determine definite limits for the pressure conditions that will occur in particular systems, it becomes necessary to assume that the extreme conditions that can occur in any system may occur in particular systems, in order to determine minimum requirements for the prevention of backflow or backsiphonage for general application to all plumbing systems under all conditions of service. This assumption is equivalent, as will develop later, to the assumption that the maximum effects possible from any vacuum, in combination with the atmospheric pressure acting through the supply openings of the system, may be encountered at some time in any particular up-feed supply system.

2. MAXIMUM EFFECTS OF VACUA AND PRESSURE CONDITIONS IN WATER-SUPPLY SYSTEMS

Acting on the preceding assumptions, we may proceed with an analysis of the effects of vacua as they apply to different types of cross-connections. The maximum or limiting cases are not dependent on direct or simple siphon action, as the term siphon action is commonly understood, but on certain phenomena connected with the maximum rate of air-flow through the various types of supply openings presented in the plumbing systems.

(a) FLOW OF AIR THROUGH ORIFICES

The theory of the flow of gases through orifices at high velocities has been fully developed by other investigators, so the subject may be introduced here by the statement of certain facts proved by experiment and generally accepted.

It is an accepted fact that rate of flow of air through an opening from the free atmosphere at a pressure P_a into an inclosed space (tank or water-supply system) at a lower pressure P_r increases as P_r is decreased until a critical pressure ratio $r_c=P_r/P_a$ is reached, after which the mass rate of flow remains sensibly constant as the ratio P_r/P_a is reduced below the critical ratio. In the range of pressure ratios $r_c>P_r/P_a>0$, the velocity of flow in the minimum section or vena contracta of the jet is equal to the velocity of sound in air at the pressure and density of the air in the minimum section of the jet.

This phenomenon of critical flow of gases has a direct application in two phases of the problem: (1) The maximum effect it can exert in lifting water across a vertical air gap into a water-supply opening, and (2) the maximum effect it can exert in lifting water in the submerged portion of a partially submerged outlet to a point where it can mix with the stream of air flowing through the unsubmerged part, the maximum effects in both cases being determined by the maximum rate of air-flow.

(b) SAFE AIR GAP

Water may be lifted across a vertical air gap into the water-supply lines by the combined effect of the atmospheric pressure and a vacuum in the supply system, as illustrated in figure 9, in which the glass jar represents an open-top plumbing fixture, the glass tube represents a faucet spout and the evacuated tank to which the tube is connected represents an evacuated water-supply system. The safe air gap will be defined as the minimum vertical distance x across which water cannot be lifted by the effects of atmospheric pressure in combination with the vacuum in the tank (see fig. 9). The problem is to determine the minimum safe gap x in terms of the dimensions of the faucet for the maximum (critical) flow of air through the faucet.

(c) SAFE PARTIALLY SUBMERGED SUPPLY OUTLETS

Again the maximum (critical) backflow of air into the supply system serves as a means of determining the safety of a partially submerged supply outlet under all possible service conditions. (See fig. 5.) In this connection, a relation or principle of arrangement that applies to and determines the limit of effectiveness of all partially submerged supply outlets may be pointed out. This arrangement

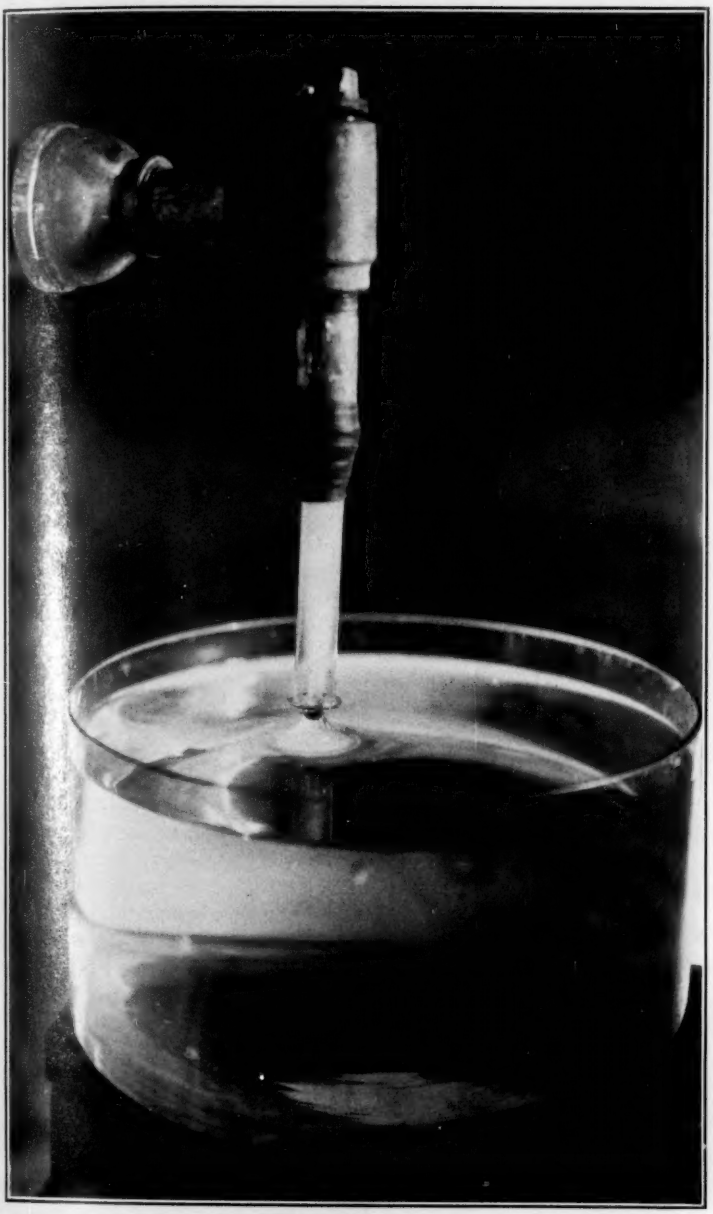

FIGURE 9.—*Backflow across an air gap.*

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may be described as two orifices in series, one an inner passage leading from the flush chamber to the supply branch, indicated in figure 18 by the symbol i, and the other an outer orifice leading from the flush chamber to the outer air, indicated by the symbol O, either or both of which orifices may be a single or multiple passage. There is also a third passage leading from the fixture to the flush chamber, this one submerged, through which backflow of water may take place under certain conditions.

Practically any indirect cross-connection may be considered as a modification of the arrangement described. In the case of a jet water closet with flush-valve supply, the passage through the flush valve forms the inner orifice, the rim ports the outer orifice, and the jet passage the submerged third opening. In the case of an air gap, the passage through the valve is the inner orifice, the passage over the water surface to the faucet spout the outer orifice, and the space over the water surface directly under the faucet spout corresponds to the submerged inlet.

The special application of this combination of two orifices in series and a submerged outlet which is of immediate interest and which lends itself to a definite analysis is the device commonly known as a siphon-breaker or vacuum-breaker. The effectiveness of the device in the prevention of backflow from a plumbing fixture is determined by the relative cross sections of the inner and outer orifices and the height to which water can rise in the submerged outlet before it mixes with the air stream flowing back into the water-supply system. Effectiveness is defined, and methods of determining the effectiveness of the device are given in the next section of the paper.

IV. MAXIMUM EFFECTS OF VACUA AND MINIMUM REQUIREMENTS FOR PREVENTION OF BACKFLOW

The preceding section of this paper contains a descriptive analysis of the conditions that may occur in water-supply systems in respect to their limits, and of the effects of these conditions in producing backflow or backsiphonage. This section gives a more detailed theoretical and experimental analysis of a number of special phenomena and physical problems associated with the general problem of preventing backflow, including: (1) The limit in rate of evacuation in water-supply lines; (2) safe air gaps for prevention of backflow; (3) effectiveness of siphon-breakers in preventing backflow; (4) classification of commercial siphon-breakers; (5) tests for effectiveness; and (6) stability of flush valves as related to backsiphonage. As previously stated, these different phenomena and the problems growing out of them are related mainly through their association in the plumbing systems and are, therefore, treated here as separate problems. The reader who is already familiar with or who does not care to give the time to a critical reading of the mathematical analyses of these problems may pass immediately to the summary of the results at the beginning of section V without breaking the continuity of the descriptive analysis of the problem as a whole.

1. RATE OF EVACUATION—MAXIMUM LIMIT

As stated in Section III of this paper, the evacuated volume and the rate of evacuation at any time in a water-supply system are

exactly equal to the volume of water displaced from the system and to the volume rate of displacement of the water, respectively. It is impossible to compute the maximum rate of displacement that can occur in any particular system, because of its complexity and because of the impossibility of determining the minimum pressure that will occur in that system. However, if we know the diameter of the main water-supply pipe (service pipe) of the building, we can determine by applying simple hydraulic principles an upper limit to the possible volume rate of displacement in terms of the pipe diameter, as will be shown in the following section. The maximum velocity of evacuation thus determined will not be exceeded in any building water-supply system whatever.

(a) TERMINAL VELOCITY

In any piping system filled with a liquid at rest, if we suddenly apply a definite pressure difference to the system and maintain it unchanged, the liquid will be accelerated, and the mean velocity of flow will approach asymptotically a constant value, reaching it when the frictional resistance opposing the flow becomes equal to the forces—pressure and gravitational—tending to produce flow.

As will be shown presently, the particular case of pipe flow in which we are interested here is that of flow out of a vertical pipe open at the top, the pipe being filled initially with water at rest, after which a valve at the bottom is opened suddenly, and the water is allowed to flow out freely into the atmosphere under the action of gravity. When the valve is opened, the column of water accelerates until, if the pipe is long enough, it attains a constant velocity for which the frictional force opposing flow is equal to the gravitational force producing flow, and falls thereafter at this constant velocity until the pipe is empty. This maximum velocity of fall attained by the water column will be called the "terminal velocity" for the pipe. It will be shown later that the maximum rate of evacuation of a water-supply system in a building is determined by the terminal velocity for the pipe used in the system. Correspondingly, the distance that the water falls in the pipe before attaining the terminal velocity will be called the "terminal length" of the pipe for the assumed conditions.

(b) METHOD OF DETERMINING TERMINAL VELOCITIES IN BUILDING SUPPLY SYSTEMS

The customary rational formula for computing the velocity of flow in a pipe line may be expressed in the form:

$$\frac{H}{L}=\lambda\frac{l}{d}\frac{v^2}{2g}, \tag{1}$$

where

H=the loss of head in the length L feet of pipe, measured in feet of the liquid flowing,
d=the diameter of the pipe in feet,
v=the mean velocity of flow in ft/sec,
g=the acceleration of gravity in ft/sec^2, and
λ=a dimensionless friction factor that depends only on the Reynolds number for smooth-walled pipe.

This equation enables us to compute the loss of head due to friction in a straight pipe of uniform diameter d and of length L between any two measuring sections between which the mean velocity is v, provided we know the correct value of λ that should be used. Or conversely, if we have a definite length of pipe L, and if there is available a definite head H to produce flow, we can compute the velocity that will result. It is clear from the equation that, the greater the value of the ratio H/L (called the "hydraulic gradient"), the greater will be the velocity of flow in the system, and our problem is to determine what conditions that may be encountered in building supply systems will produce the highest velocity of evacuation of the system; or, in other words, the greatest value of H/L that may occur under service conditions.

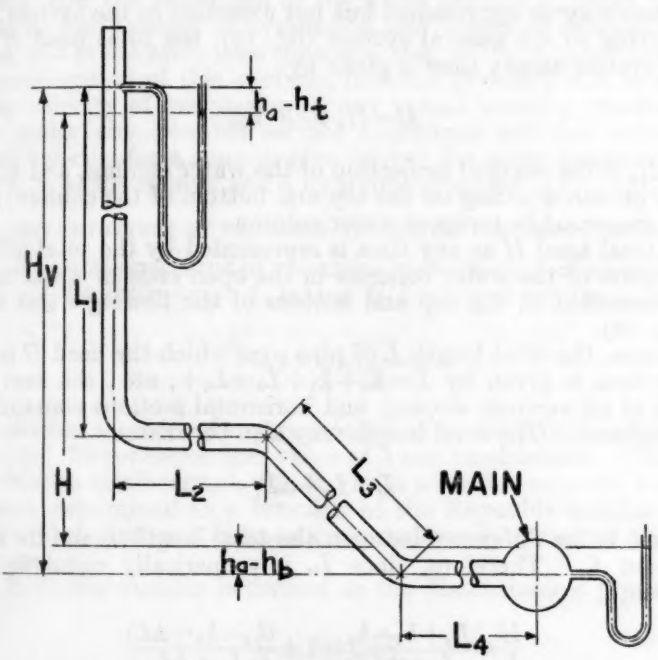

FIGURE 10.—*Diagrammatic sketch illustrating main riser and service pipe for building supply system.*

For the purpose of analyzing the conditions that may occur in the water-supply system of a building relative to the maximum value of H/L, we assume a general layout (fig. 10) in which: (1) The system may consist of a single vertical line of the same diameter throughout, or it may consist of any number of vertical, horizontal, and sloping sections of the same diameters connected by elbow bends; (2) the pipe may be either open or closed at the top and may be open at the bottom or connected by a service pipe to a street main or other source of supply; and (3) the pipes are originally filled with water.

If we now assume a sudden and complete failure in the supply pressure produced by a break in the street main or service pipe, a shut-

down in a pumping system, excessive water demands on the main supply, or other comparable cause, water will flow from the system, accelerating until it approaches the terminal velocity for the system, as given by eq 1.

We note from eq 1 that the velocity v varies directly as the square root of the hydraulic gradient H/L and the diameter d of the pipe and inversely as the square root of the friction factor λ. Perfectly smooth pipe has the lowest possible friction factor, and therefore smooth pipe will yield the highest terminal velocity, the factors H/L and d remaining constant for the comparison. Similarly, the velocity v increases as d increases; and, therefore, if the building supply piping is not greater in diameter than the service pipe, the usual form of installation, the terminal velocity determined from the maximum possible value of H/L for a system of the same diameter as the service pipe will set a limit that may be approached but not exceeded in the system.

Referring to the general system (fig. 10), the total head H acting on the system at any time is given by

$$H=H_v+h_t-h_b, \tag{2}$$

where H_v is the vertical projection of the water column, and h_t and h_b are the pressures acting on the top and bottom of the column, respectively, measured in terms of water column.

The total head H at any time is represented by the total difference in elevation of the water columns in the open ends of water manometers connected at the top and bottom of the flowing water column (see fig. 10).

Likewise, the total length L of pipe over which the head H is acting at any time is given by $L=L_1+L_2+L_3+L_4+$, etc., the sum of the lengths of all vertical, sloping, and horizontal sections containing the water column. The total length may also be written

$$L=L_v+\Delta L,$$

where ΔL is the difference between the total length L and its vertical projection L_v. Therefore, since L_v is numerically equal to H_v by definition,

$$\frac{H}{L}=\frac{L_v+h_t-h_b}{L_v+\Delta L}=1+\frac{(h_t-h_b-\Delta L)}{L_v+\Delta L} \tag{3}$$

Obviously, H/L in any system will be greater or less than unity as h_t-h_b is greater or less than ΔL, and will be equal to unity when $\Delta L=0$ and $h_t=h_b$ and when $h_t-h_b=\Delta L$.

If the system is closed at the top (unvented), H/L must be less than unity regardless of the form of the system, since h_t will equal h_v if water flows out of the system, and h_b cannot be less than h_v.

If the system is open at the top (completely vented), again H/L must be less than unity, unless h_t-h_b is numerically greater than ΔL. Since h_t must be sensibly less than atmospheric pressure (h_a=34 feet of water column, approximately), and h_b cannot be less than h_v, ΔL must be considerably less than 34 feet in any system, to make H/L=1. In the practical case, ΔL will include the offset of the main riser from the street water main, which will usually in itself be greater than 34

feet. Furthermore, the loss of head due to the flow of the water around the bends in the system is very considerable at velocities approaching the terminal velocity in the system and has the same effect on the value of H/L as increasing ΔL.

The maximum possible value of H/L would occur when $\Delta L=0$, a value given only by the impractical case of a completely vertical vented system connected directly to a water main without offset at its base. Even in this case, h_t-h_b will be less than h_a-h_e, since h_t must be less than h_a, and h_b cannot be reduced to h_e with water flowing from the building supply system into the water main at a high velocity. Furthermore, if the piping system is long enough for the velocity of evacuation to approach closely the terminal velocity for a hydraulic gradient of $H/L=1$, any possible value of h_t-h_b will be negligible compared with the projection of the water column L_v, since h_t must decrease as the velocity of evacuation and length of evacuated pipe increase, and at the same time the value of h_b will tend to increase.

In consideration of this analysis, it seems perfectly safe to assume that the velocity of evacuation of any actual building water-supply system under any possible service conditions will not exceed the terminal velocity for a smooth pipe having the same diameter as the service pipe of the system and a hydraulic gradient of $H/L=1$.

(c) DETERMINATION OF TERMINAL VELOCITIES FOR VERTICAL PIPES

The assumed upper limit of velocities of evacuation of water-supply systems will be given by eq 1, taking $H/L=1$, and writing v_t for v:

$$\frac{H}{L}=\lambda\times\frac{1}{d}\times\frac{v_t^2}{2g}=1 \tag{4}$$

The obvious method of determining v_t is to solve this equation for v_t, provided the corresponding value of λ can be obtained. The value of the friction coefficient, λ, which varies with the velocity, has been accurately determined as a function of the Reynolds number R_e for smooth-walled pipe and is known approximately for some classes of rough pipe.

The Reynolds number is defined as the dimensionless product

$$R_e=\frac{dv\rho}{\mu}=\frac{dv}{\nu}, \tag{5}$$

where

ρ=the density of the fluid flowing,
μ=its absolute viscosity, and
ν=its kinematic viscosity ($=\mu/\rho$).

A unique relation exists between λ and R_e for the flow of an incompressible viscous fluid through a smooth pipe, which can be expressed mathematically as

$$\lambda=\text{function}\left(\frac{dv}{\nu}\right). \tag{6}$$

This means that the relation between λ and the Reynolds number can be represented by a single curve for smooth-walled pipe. Figure 11 shows this relation between the friction factor and the Reynolds

number dv/ν in the turbulent region for smooth pipes and is based on many experiments with different fluids [20–21].

(1) *Terminal velocities in smooth pipes.*—The terminal velocities for smooth-walled pipes 1, 2, 3, 4, and 6 inches in diameter were computed from eq 4, using values of λ taken from figure 11. Since v_t appears in the Reynolds number, the equation cannot be solved directly for v_t, and it is necessary to use the method of successive approximations. A value of v_t was assumed for a trial computation of the Reynolds number, and the corresponding value of λ was read from figure 11. Using this value of λ, a new value of v_t was

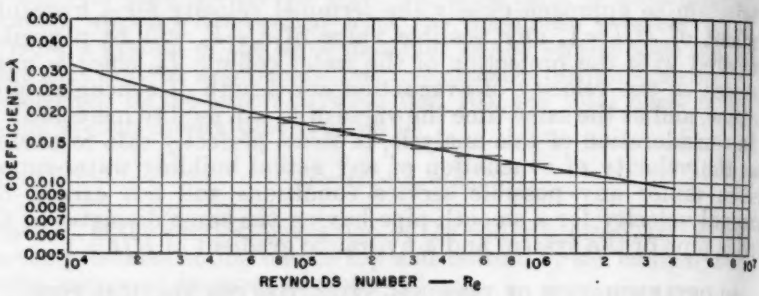

FIGURE 11.—*Friction factor λ as a function of the Reynolds number.*

computed by this equation. This new value of v_t was then used to compute a new Reynolds number, and the process was repeated until the last two values of v_t computed from the equation agreed with each other within the accuracy with which λ could be read from the curve. These computed terminal velocities for vertical smooth pipe from 1 to 6 inches in diameter are given, together with other pertinent data in table 1 and are plotted in figure 12.

TABLE 1.—*Terminal velocities, terminal lengths, and maximum rates of displacement for smooth, vertical pipes*

Diameter		Volume per foot length of pipe		Terminal velocity	Rate of displacement		Length required to attain 0.99 terminal velocity	
Nominal	Actual						Approx. (eq 13)	Exact method
in.	in.	cu ft	gal	fps	cfs	gpm	ft	ft
1	1.049	0.006	0.045	18.45	0.111	49.8	20.8	21.9
2	2.067	.023	.172	28.5	.664	299	49.2	52.6
3	3.068	.051	.382	37.3	1.91	861	84.8	88.4
4	4.026	.088	.659	44.3	3.92	1,760	119.4	124.1
6	6.065	.201	1.50	57.2	11.5	5,160	198.5	204.0

(2) *Terminal velocities in rough pipes.*—The $\lambda - R_e$ relation for rough pipes is not a single curve, as represented in figure 11 for smooth pipe. For any given class of rough pipes, a separate curve is obtained for each diameter of pipe, giving an approximately parallel series of curves covering a band in the $\lambda - R_e$ diagram. The reason that the curves for pipes of different sizes do not coincide is that the relative hydraulic roughness varies with the diameter. For these reasons, the loss in head per unit length of pipe for a given velocity of flow cannot be

predicted for rough pipe from past experience as accurately as for smooth pipe. However, the $\lambda - R_e$ curves for very rough pipe show one characteristic not shown by the curves for smooth pipe; the curves become horizontal for high Reynolds numbers, yielding a constant value of λ in the region of high velocities.

As a matter of general information, the terminal velocities in a number of sizes of very rough pipe were computed from values of λ taken from experiments on rough pipe [22] and are plotted in figure 12.

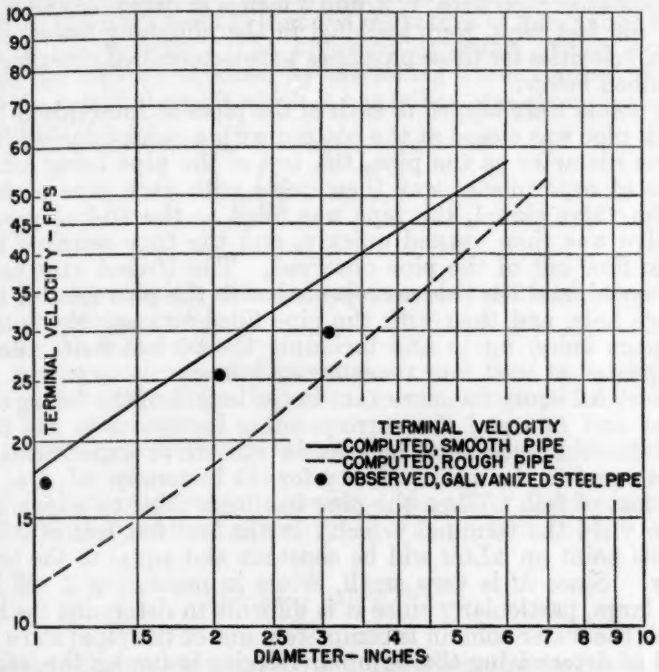

FIGURE 12.—*Terminal velocities for pipes 1 to 6 inches in diameter.*

(3) *Terminal velocities in brass, copper, and steel pipes.*—The friction factors for smooth copper or brass tubing with streamline fittings will differ but slightly from the values given in figure 11 for smooth pipe. Threaded brass or steel pipe may be expected to give $\lambda - R_e$ curves lying above the curve for smooth pipe; but, if the joints are carefully made, the curves will approach very closely the curve for smooth pipe. Experiments with steel pipe by different experimenters show a considerable variation in the $\lambda - R_e$ curves, probably in part owing to differences in installation and in the technique of measurement. However, the $\lambda - R_e$ curves for some of the more recent experiments on 4-inch galvanized-steel pipe[4] lie close to the curve for smooth pipe, indicating the probability that a smoother grade of pipe is now being manufactured than in the past. (See also reference 23.)

[4] Unpublished data by the authors.

(d) EXPERIMENTAL DETERMINATION OF TERMINAL VELOCITIES IN VERTICAL GALVANIZED-STEEL PIPES

The experimental determination of terminal velocities in open-ended vertical pipes requires long vertical pipes, and the existence of a plumbing tower 10 stories high at the National Bureau of Standards made the erection of such test lines for a limited range of diameters a simple matter. Hence, to demonstrate the validity of the statement made earlier in this paper that the rational pipe-flow equation could be used to compute terminal velocities in vertical pipes, galvanized-steel pipe lines, 1, 2, and 3 inches in diameter and approximately 100 feet high, were installed in the plumbing tower, and the terminal velocities for these pipe lines were determined experimentally, as described below.

Gage points were tapped in each of the pipes at intervals of 10 feet, and each pipe was closed at the bottom with a quick-opening valve of the same diameter as the pipe, the top of the pipe being left open. A series of experiments was then made with each pipe as follows: With the valve closed, the pipe was filled to the 10-foot gage hole. The valve was then opened quickly, and the time required for the water to flow out of the pipe observed. The 10-foot gage hole was then plugged, and the process repeated with the pipe filled to the 20-foot gage hole, and then with the pipe filled successively to the different gage holes, up to and including the 90-foot hole. Readings were repeated at least four times for each level.

If we let ΔL equal the increment in the length of the falling column of water and Δt equal the corresponding increment in the time of descent for the successive lengths in successive experiments, then $\Delta L/\Delta t$ is equal to the mean velocity for the increment ΔL, i. e., in the last 10 feet of fall. When the pipe has been filled to a high enough point to yield the terminal velocity in the last few feet of fall, then from this point on $\Delta L/\Delta t$ will be constant and equal to the terminal velocity. Since Δt is very small, errors in measuring it will be relatively large, particularly since it is difficult to determine the instant at which the water column is completely out of the pipe; and a better method of determining the terminal velocity is to plot the lengths of the descending columns as ordinates and the time of descent as abscissas. This will give a straight line in the region where the column is flowing at the terminal velocity, and the slope of the line will give the terminal velocity.

The terminal velocities determined in this way are plotted in figure 12 for comparison with the results computed for smooth pipes and for one class of very rough pipes, as described in sections IV-1-(c)-(1) and (2) of this paper.

Since these experimental values for galvanized pipe fall between the terminal velocities for smooth pipe and rough pipe, as they should, and since the problem is merely to set a limit for the maximum rate of evacuation of water-supply systems, it will be assumed that the velocity of evacuation in any practical water-supply system cannot exceed the terminal velocity of flow in a vertical smooth pipe of the same diameter as the service pipe of the water-supply system in question. The smooth-pipe curve in figure 12 can then be used to determine the terminal velocities for vertical pipes over the range of diameters given.

(c) TERMINAL LENGTHS

In addition to knowing what terminal velocities can be attained in vertical pipes of various diameters, it is important to ascertain whether the buildings in which vertical supply lines are constructed are high enough to permit these terminal velocities to be attained. This can be done with the aid of an equation developed in an earlier publication [24]. In deriving this equation, it is assumed (1) that the vertical pipe is wide open at both ends, so that atmospheric pressure (approximately) acts on the top and the bottom of the column making $h_i = h_o$ as nearly as possible, (2) that the cross section of the pipe remains full during the flow, and (3) that the resistance to flow varies with the square of the velocity. The following equation, giving a relation between the velocity attained by the falling water column as a function of the height through which it has fallen, was given in the earlier publication [24]:

$$v = \left(\frac{g}{k} - \frac{\frac{g}{k} - v_0^2}{e^{+2kS}} \right)^{1/2}, \tag{7}$$

where

v = the velocity attained after a fall through the vertical distance S,
v_0 = the initial velocity (when $S=0$),
g = the acceleration of gravity,
e = the base of the Naperian system of logarithms (=2.7183), and
k = a friction factor which depends on the diameter and roughness of the pipe.

In the case that we have to consider, the water column starts from rest; hence $v_0=0$, and we can write eq 7 as

$$v = \left(\frac{g}{k}\right)^{1/2} (1 - e^{-2kS})^{1/2}. \tag{8}$$

Obviously the velocity of flow approaches the terminal velocity asymptotically; and, strictly speaking, the water column would have to fall through an infinite distance before it would attain its terminal velocity. Actually the velocity of fall approaches the terminal velocity so rapidly that the latter is reached, as nearly as can be measured, in a comparatively short length of pipe. An approximate value of this length for any given diameter of pipe can be obtained from eq 8 in the following manner. If we substitute S=infinity in the equation, the exponential term becomes zero and we have for the terminal velocity

$$v_t = (g/k)^{1/2}. \tag{9}$$

Now, if we agree arbitrarily to assume that the terminal velocity has been reached when the term $(1-e^{-2kS})^{1/2}$ in eq 8 has reached some value slightly less than 1, say 0.99, we can compute from this equation a finite value of S for a given value of k. Since values of k for different pipe diameters and roughnesses are not available, however, it will be convenient to replace k in terms of the pipe diameter d and the commonly used dimensionless friction coefficient λ, for which values are

readily available for many kinds of pipe, particularly smooth pipe. From eq 9 we have

$$kv_t^2/g=1, \tag{10}$$

and, equating the left member of this last equation to the left member of eq 4, there results:

$$k=\lambda/2d, \tag{11}$$

and this value of k can be substituted back in eq 8 to give this equation the more convenient form

$$v=(2gd/\lambda)^{\frac{1}{2}}(1-e^{-\lambda S/d})^{\frac{1}{2}}. \tag{12}$$

Approximate values of the terminal lengths for smooth pipes ranging from 1 to 6 inches in diameter have been computed from the relation

$$(1-e^{-\lambda S/d})=0.99,$$

arranging this in the more convenient form

$$S=3.913\frac{d}{\lambda}, \tag{13}$$

and using a value of λ corresponding to the terminal velocity for the pipe in question. The values thus computed are given in table 1.

This method of computing terminal lengths is not exact, since λ varies considerably during the acceleration of the water column. Hence, although it is not important to determine these lengths with great accuracy, they were recomputed by a more nearly exact method, based on the differential equation from which eq 7 was derived, taking into account the variation of λ. These values of the terminal length are also given in table 1, and it will be observed that they are a little larger than the values yielded by eq 13.

This latter method of computation affords a simple and accurate method of computing the entire fall curve (distance through which the column has fallen plotted against the instantaneous velocity of fall). Consequently, these curves were computed for smooth pipes 1, 2, 3, 4, and 6 inches in diameter, in order to illustrate the rapidity with which the column of water approaches its terminal velocity. These curves are given in figure 13, together with the experimental data obtained for 1-, 2-, and 3-inch galvanized-steel pipe, as described in section IV–1–d of the paper.

The points plotted for these last three pipes do not represent the actual experimental data. As has already been explained, it was impossible to avoid making relatively large errors in measuring the time of fall when the height of fall was not very large. Consequently, the experimental data could not be relied on to give the form of the fall curves during the first part of the fall of the column. Hence this portion of the fall curve for each of the three pipes was computed by a method of approximations, working backward from the higher portion of the curve, which was obtained experimentally with reasonable accuracy. The points plotted are those for which the above-men-

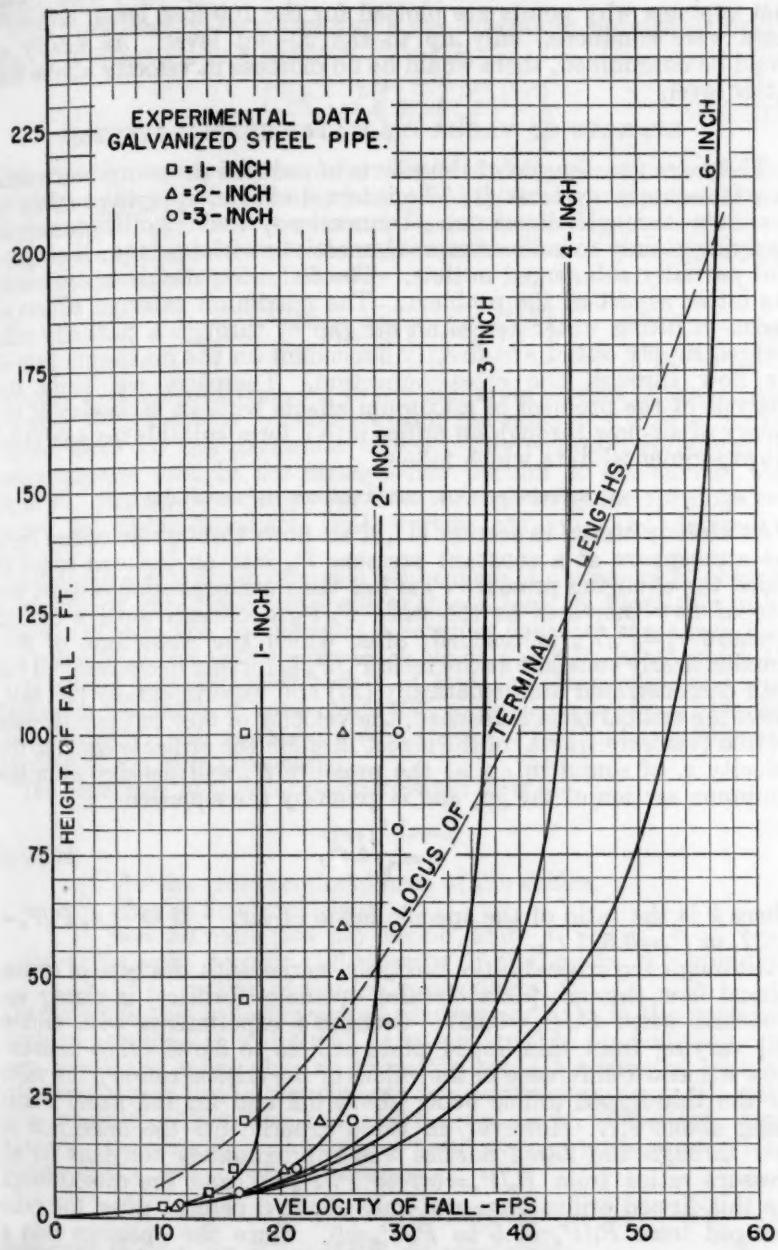

FIGURE 13.—*Fall curves for water columns in smooth vertical pipes 1 to 6 inches in diameter.*

tioned computations were made and yield curves that coincide accurately with the higher portion of each corresponding fall curve. This fact explains why points are plotted for the 100-foot level, although tests were conducted only up to the 90-foot level. As nearly as could be determined, there would be no increase in velocity above this latter level.

2. EFFECTS OF VACUA ON WATER-SUPPLY SYSTEMS

There are two aspects of the effects of reduced pressures and vacua in water-supply systems (1) The internal effects, applying mainly to backflow through direct cross-connections, and (2) the external, applying mainly to indirect cross-connections with inadequate air gaps and partially submerged outlets. The following discussion refers to the latter aspect of the problem. The maximum external effects of vacua in lifting water across an air gap or through a partially submerged supply outlet are directly dependent on the maximum rate of air flow through the cross-connection. Therefore we begin the analysis of the problem of maximum effects with an extension of the theory of air-flow through an orifice into a form suitable for analyzing the experimental data which follow.

(a) EXTENSION OF THE THEORY OF AIR-FLOW

As already stated in section III, if air flows through an orifice from the atmosphere at a constant pressure P_a into an inclosed space in which the changing pressure P_r is less than atmospheric pressure, the rate of flow increases as the ratio P_r/P_a decreases until a critical pressure $r_c=P_r/P_a$ is reached, after which the mass rate of flow remains nearly constant as the ratio P_r/P_a is further decreased. It has been demonstrated mathematically [24] and experimentally [25] that, when the critical ratio is reached, the velocity of flow in the minimum section (vena contracta) of the air jet through the orifice is equal to the velocity v_s of sound in air at the pressure P_c and density ρ_c in the minimum section of the jet, and is given by the equation

$$v_s=\sqrt{\frac{P_c k}{\rho_c}},$$

where k is the ratio of the specific heats of air. If $k=1.4$, $P_c/P_a=0.527$, or $P_c=0.527\ P_a$.

Although the critical ratio $P_r/P_a=r_c$ varies with the type of orifice, critical flow through plain circular openings (orifices) is closely approached when $P_r/P_a=0.527$. Stanton's experiments with orifices [25] varying from thin-lipped plate orifices to flared tubes (nozzles) show a marked difference in the values of the critical ratio r_c, the value for the thin-lipped orifice being about 0.2 and for the flared nozzle being about 0.7. However, in these experiments the mass rate of flow through the flared nozzles was approximately constant for all pressure ratios from $P_r/P_a=0.7$ to $P_r/P_a=0$, and the rate through the thin-lipped orifice increased only about 6 percent when the ratio changed from $P_r/P_a=0.5$ to $P_r/P_a=0$. Since the openings into a supply system cover an intermediate range between the extreme types used by Stanton, it seemed advisable to study experimentally the characteristics of air-flow through openings such as presented by faucets, flush valves, siphon-breakers, etc., in order to verify the existence of a critical ratio for these types of irregular orifices and to

determine its approximate value for each. The data given later show that a critical ratio of $P_r/P_a=0.5$ or greater exists for the various types employed.

The equation for the velocity of a gas expanding through an orifice from a pressure P_a to a pressure P_r is [27]

$$v=\sqrt{\frac{2k}{k-1}\times\frac{P_a}{\rho_a}\left[1-\left(\frac{P_r}{P_a}\right)^{\frac{k-1}{k}}\right]}. \tag{14}$$

This equation is general except for the effect of any shape or size factors relating to the orifice. It may be applied therefore to the special case of air expanding from the pressure P_a (atmospheric pressure) to the pressure P_c, the pressure in the minimum section of the jet through the orifice, and becomes in this case

$$v_c=\sqrt{\frac{2k}{k-1}\times\frac{P_a}{\rho_a}\left[1-\left(\frac{P_c}{P_a}\right)^{\frac{k-1}{k}}\right]}, \tag{15}$$

in which v_c is the local velocity in the minimum section of the jet, this velocity being sensibly constant within the range $0<P_r/P_a<r_c$, the critical ratio for the particular orifice. The equation employed for analyzing the data in the straight-line portion of the curves, that is, in the critical flow range, for flow through irregular openings presented by siphon-breakers, flush valves, etc., may be derived as follows.

Assuming a flow of air from the atmosphere at a pressure P_a through some type of small opening (orifice) into a tank in which the initial pressure is zero, the gas flows at a sensibly constant mass rate until the pressure in the tank reaches a value of $P_r=r_cP_a$, after which the mass rate of flow decreases slowly at first, and then more and more rapidly as the ratio of pressures P_r/P_a approaches unity, where flow ceases entirely. An equation giving the ratio P_r/P_a at any time as a function of the time t is desired.

The mass rate in this range of constant flow is

$$m=CA\rho_cv_c, \tag{16}$$

in which

A=the cross-sectional area of the orifice,
C=the flow coefficient,
m=the mass flow per second, and
ρ_c and v_c=the density and velocity of the air in the minimum section of the jet, respectively.

The factors in this equation are all sensibly constant in the particular range of pressures in which the equation is to be applied, using the term *sensibly* to mean that no variation could be detected with the instruments used in the experiments to observe or measure the quantities involved. Therefore, the total mass of air M_r in the tank at any time will vary directly with the time t and we may write, since V_r, the volume of the receiving tank is constant,

$$M_r=\rho_rV_r=mt=CA\rho_cv_ct. \tag{17}$$

Now from the gas law $PV=MRT$, we may write

$$P_rV_r=M_rRT_r, \tag{18}$$

where P_r, V_r, M_r, and T_r are, respectively, the pressure, volume, mass, and absolute temperature in the tank at any time, and R is the gas

constant. We may also write for the same mass at atmospheric pressure P_a:

$$P_aV_a=M_rRT_a. \tag{19}$$

Dividing eq 18 by eq 19:

$$\frac{P_rV_r}{P_aV_a}=\frac{T_r}{T_a}. \tag{20}$$

Also for the same mass,

$$V_r/V_a=\rho_a/\rho_r,$$

and T_r may be written

$$T_r=T_a-\Delta T;$$

from which by substitution in eq 20:

$$\frac{P_r\rho_a}{P_a\rho_r}=\left(1-\frac{\Delta T}{T_a}\right) \tag{21}$$

Multiplying each member of eq 17 by the corresponding member of eq 21:

$$\frac{P_r}{P_a}\times\frac{\rho_a}{\rho_r}\times\rho_rV_r=CA\rho_cv_ct\left(1-\frac{\Delta T}{T_a}\right), \text{ or}$$

$$P_r/P_a=\frac{CA}{V_r}\frac{\rho_c}{\rho_a}v_ct\left(1-\frac{\Delta T}{T_a}\right), \tag{22}$$

Substituting $A=\frac{\pi d^2}{4}$ and for v_c its value from eq 15, where d is the diameter of the orifice,

$$\frac{P_r}{P_a}=\frac{C\pi d^2}{4V_r}\times\frac{\rho_c}{\rho_a}\sqrt{\frac{2k}{k-1}\times\frac{P_a}{\rho_a}\left[1-\left(\frac{P_c}{P_a}\right)^{\frac{k-1}{k}}\right]}\left(1-\frac{\Delta T}{T_a}\right)t. \tag{23}$$

Now

$$\frac{\rho_c}{\rho_a}=\left(\frac{P_c}{P_a}\right)^{\frac{1}{k}} \text{ and } P_a=\rho_agh'_a,$$

where h'_a is the height of a hypothetical atmosphere of uniform density ρ_a giving the pressure P_a. Substituting these values in eq 23, there results

$$\frac{P_r}{P_a}=\frac{C\pi d^2}{4V_r}\sqrt{gh'_a}\sqrt{\frac{2k}{k-1}\left(\frac{P_c}{P_a}\right)\left[1-\left(\frac{P_c}{P_a}\right)^{\frac{k-1}{k}}\right]}\left(1-\frac{\Delta T}{T_a}\right)t \tag{24}$$

or

$$\frac{P_r}{P_a}=r=\frac{C\pi N}{4}\times\frac{d^2\sqrt{gh'_a}}{Vr}\left(1-\frac{\Delta T}{T_a}\right)\times t, \tag{25}$$

where

$$N=\sqrt{\frac{2k}{k-1}\left(\frac{P_c}{P_a}\right)^{2/k}\left[1-\left(\frac{P_c}{P_a}\right)^{\frac{k-1}{k}}\right]}.$$

(b) EXPERIMENTAL STUDY OF THE FLOW OF AIR THROUGH PLATE ORIFICES, SIPHON-BREAKERS, AND FLUSH VALVES

Equation 25 was employed in the study of critical flow through irregularly shaped orifices as follows:

The apparatus used in making these tests consisted of a vacuum tank of 318 gallons capacity, a vacuum pump capable of reducing the pressure in the tank to less than 4 inches of mercury absolute pressure (about 26 in. of mercury below atmospheric pressure) in a reasonably

short time, a manometer for measuring the pressure in the tank at any time, a 2-inch gate valve connected to the tank by a short nipple, and fittings for mounting the various orifices. See figures 25 and 26, showing a siphon-breaker mounted on the same fittings.

The tank was evacuated for each test with the gate valve closed and the orifice or other device mounted in the end of a 2-inch pipe. Then the pump was shut off, and the initial pressure P_o in the tank recorded. Next the gate valve was opened, and the time intervals from the opening of the valve to the instants at which the pressure in the tank reached successive selected values between $P_r = P_o$ and $P_r = P_a$ were observed.

From these data there were obtained a series of ratios r_1, r_2, r_3, etc., and the corresponding time intervals t_1, t_2, t_3, etc., required to reach these ratios from the initial condition.

Three circular square-edged orifices of 0.125 inch (0.0104 ft), 0.250 inch (0.0208 ft), and 0.500 inch (0.0417 ft) diameters were drilled in circular disks cut from ⅛-inch brass plate and were tested as just described. The purpose of testing these plate orifices was to provide characteristic curves for a simple, easily reproduced form of orifice with which the curves obtained for the irregular and tortuous passages of siphon-breakers and flush valves could be compared. The data obtained are given in table 2.

TABLE 2.—*Data for thin-plate orifices*

t	Δt	$t_o = t + \Delta t$	$\frac{d^2\sqrt{gh'_a}}{V_r} \times 10^3$	$\frac{d^2\sqrt{gh'_a}}{V_r} \times t_o$	r
			$d = 0.125$ inch		
sec	sec	sec			
0.0	23.7	23.7	2.35	0.0556	0.029
127.9	23.7	151.6	2.35	.355	.184
239.9	23.7	263.6	2.35	.618	.322
372.4	23.7	396.1	2.35	.930	.454
465.5	23.7	489.2	2.35	1.150	.588
586.8	23.7	610.5	2.35	1.430	.724
730.9	23.7	754.6	2.35	1.770	.860
1,074.0	23.7	1,092.7	2.35	2.580	1.000
			$d = 0.250$ inch		
0.0	5.7	5.7	9.37	0.0534	0.029
30.8	5.7	36.5	9.37	.342	.184
57.3	5.7	63.0	9.37	.590	.322
84.0	5.7	89.7	9.37	.840	.454
111.6	5.7	117.3	9.37	1.100	.588
142.5	5.7	148.2	9.37	1.390	.724
179.1	5.7	184.8	9.37	1.732	.860
294.0	5.7	299.7	9.37	2.810	1.000
			$d = 0.500$ inch		
0.0 *	1.45	1.45	37.60	0.0545	0.029
7.98	1.45	9.43	37.60	.354	.184
14.66	1.45	16.11	37.60	.605	.322
21.39	1.45	22.84	37.60	.859	.454
28.24	1.45	29.69	37.60	1.117	.588
35.99	1.45	37.44	37.60	1.408	.724
44.37	1.45	45.82	37.60	1.723	.860
75.14	1.45	76.59	37.60	2.880	1.000
			$h'_a = 26{,}300$ ft. $V_r = 42.5$ cu ft.		

* These times measured by electric chronograph.

TABLE 3.—*Data for moving-part siphon-breakers*

t	Δt	$t_s=t+\Delta t$	$\frac{d^3\sqrt{gh'_s}}{V_r}\times 10^3$	$\frac{d^3\sqrt{gh'_s}}{V_r}\times t_s$	r
Siphon-breaker No. 1. (d_s=0.162 inch)					
sec	sec	sec			
0.0	48.0	48.0	4.02	0.193	0.102
13.0	48.0	61.0	4.10	.250	.132
76.0	48.0	124.0	4.03	.500	.263
142.0	48.0	190.0	3.95	.750	.398
208.0	48.0	256.0	3.91	1.000	.533
276.0	48.0	324.0	3.95	1.280	.668
352.0	48.0	400.0	3.98	1.590	.803
457.0	48.0	505.0	4.09	2.065	.937
488.0	48.0	536.0	4.12	2.210	.961
536.0	48.0	584.0	4.18	2.440	.987
590.0	48.0	638.0	----------	2.880	1.000
Siphon-breaker No. 2. (d_s=0.305 inch)					
0.0	25.0	25.0	13.80	0.345	0.184
11.0	25.0	36.0	13.88	.500	.263
29.0	25.0	54.0	13.88	.750	.398
47.0	25.0	72.0	13.88	1.000	.533
66.0	25.0	91.0	14.06	1.280	.668
87.5	25.0	112.5	14.12	1.590	.803
118.0	25.0	143.0	14.43	2.065	.937
197.0	25.0	222.0	----------	2.880	1.000
Siphon-breaker No. 3. (d_s=0.146 inch)					
0.0	64.0	64.0	3.02	0.193	0.102
99.2	64.0	163.2	3.06	.500	.263
181.5	64.0	245.5	3.05	.750	.398
265.0	64.0	329.0	3.04	1.000	.533
359.0	64.0	423.0	3.03	1.280	.668
466.2	64.0	530.2	3.00	1.590	.803
613.5	64.0	677.5	3.05	2.065	.937
811.0	64.0	875.0	----------	2.880	1.000
h'_s=26,300 ft. V_r=42.5 cu ft.					

TABLE 4.—*Data for nonmoving-part siphon-breakers*

t	Δt	$t_s=t+\Delta t$	$\frac{d^2\sqrt{gh'_s}}{V_r}\times 10^3$	$\frac{d^2\sqrt{gh'_s}}{V_r}\times t_s$	r
Siphon-breaker No. 4. (d_s=0.679 inch)					
sec	sec	sec			
0.0	7.5	7.5	66.60	0.500	0.263
3.9	7.5	11.4	65.80	.750	.398
7.7	7.5	15.2	66.00	1.000	.533
Siphon-breaker No. 5. (d_s=0.465 inch)					
0.0	8.2	8.2	30.50	0.250	0.132
8.3	8.2	16.5	30.30	.500	.263
16.2	8.2	24.4	30.70	.750	.398
24.0	8.2	32.2	31.10	1.000	.533
31.8	8.2	40.0	32.00	1.280	.668
41.0	8.2	49.2	32.30	1.590	.803
53.8	8.2	62.0	33.30	2.065	.937
121.5	8.2	129.7	----------	2.880	1.000
Siphon-breaker No. 6. (d_s=0.365 inch)					
0.0	19.7	19.7	25.40	0.500	0.263
7.4	19.7	27.1	27.70	.750	.398
20.0	19.7	39.7	25.20	1.000	.533
30.8	19.7	50.5	25.30	1.280	.668
42.5	19.7	62.2	25.55	1.590	.803
59.5	19.7	79.2	26.10	2.065	.937
107.5	19.7	127.2	----------	2.880	1.000
h'_s=26,300 ft. V_r=42.5 cu ft.					

TABLE 5.—*Data for stable flush valves*

t	Δt	$t_s=t+\Delta t$	$\frac{d^2\sqrt{gh'_s}}{V_r}\times 10^3$	$\frac{d^2\sqrt{gh'_s}}{V_r}\times t_s$	r
Flush valve No. 1. (d_s=0.29 inch)					
sec	sec	sec			
0.0	18.5	18.5	12.70	0.235	0.125
19.8	18.5	38.3	12.78	.490	.260
40.2	18.5	58.7	12.68	.745	.395
61.5	18.5	80.0	12.42	.996	.526
83.9	18.5	102.4	12.35	1.265	.661
108.5	18.5	127.0	12.35	1.570	.796
143.8	18.5	162.3	12.53	2.035	.931
164.0	18.5	182.5	12.50	2.280	.970
176.0	18.5	194.5	12.38	2.410	.984
Flush valve No. 2. (d_s=0.193 inch)					
0.0	42.5	42.5	5.88	0.250	0.132
42.0	42.5	84.5	5.82	.500	.263
85.3	42.5	127.8	5.83	.745	.395
129.0	42.5	171.5	5.80	.996	.526
165.0	42.5	207.5	6.10	1.265	.661
228.0	42.5	270.5	5.80	1.570	.796
300.0	42.5	342.5	5.94	2.035	.931
405.0	42.5	447.5	6.44	2.880	1.000
Flush valve No. 3. (d_s=0.21 inch)					
0.0	40.0	40.0	5.88	0.235	0.125
43.2	40.0	83.2	5.89	.490	.260
86.7	40.0	126.7	5.88	.745	.395
132.0	40.0	172.0	5.79	.996	.526
180.7	40.0	220.7	5.74	1.265	.661
237.8	40.0	277.8	5.66	1.570	.796
322.0	40.0	362.0	5.62	2.035	.931
368.4	40.0	408.4	5.58	2.280	.970
397.5	40.0	437.5	5.51	2.410	.984
h'_s=26,300 ft. V_r=42.5 cu ft.					

Several siphon-breakers of both the moving-part and nonmoving-part types were tested in the same manner as the plate orifices (see for example, fig. 14). The data for three different siphon-breakers of the moving-part type are given in table 3. Similarly, the data for three different siphon-breakers of the nonmoving-part type are given in table 4. The data for three different flush valves tested are given in

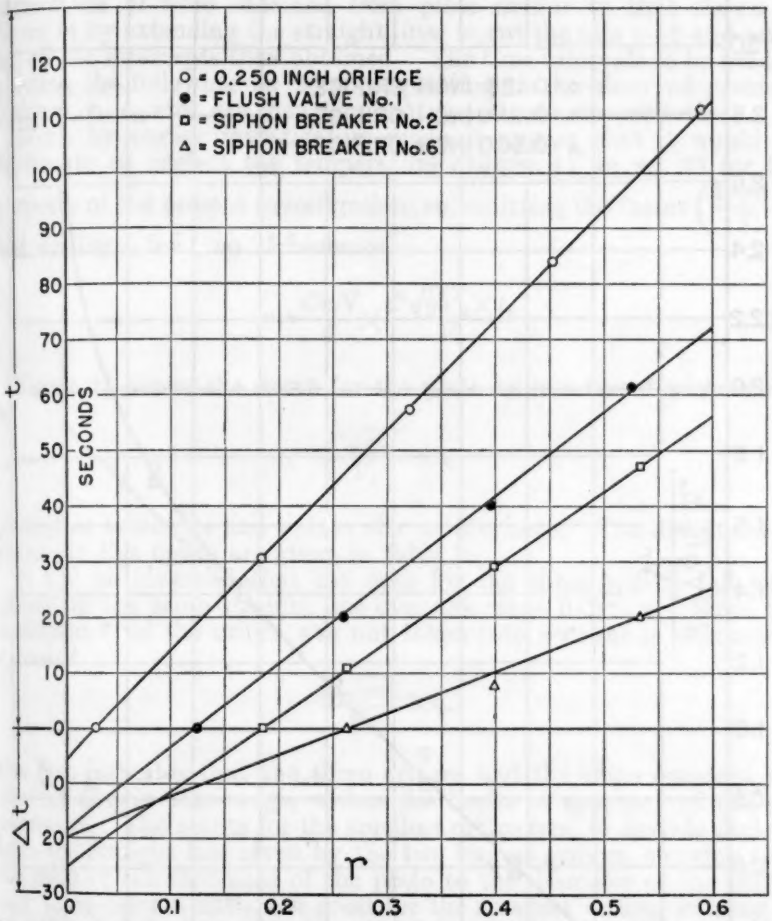

FIGURE 14.—*Air-flow through plate orifice, flush valve, and two siphon breakers in subcritical range of pressure ratio.*

table 5. (See fig. 27 for diagrammatic sketches of typical flush valves.) The data for representative devices from the above classes are plotted in figure 14 with time as ordinates and the pressure ratio r as abscissas.

Figure 14 shows that the data plotted yield straight lines, as nearly as can be determined by visual inspection, up to the highest value of r shown, indicating that the mass rate of flow is sensibly constant over the range of r plotted (subcritical range).

The plate orifice data for the entire range of r were substituted in eq 25 and were then plotted in figure 15, using the dimensionless variables

$$\frac{d^2\sqrt{gh_a'}}{V_r}\,t_0 \text{ and } r.$$

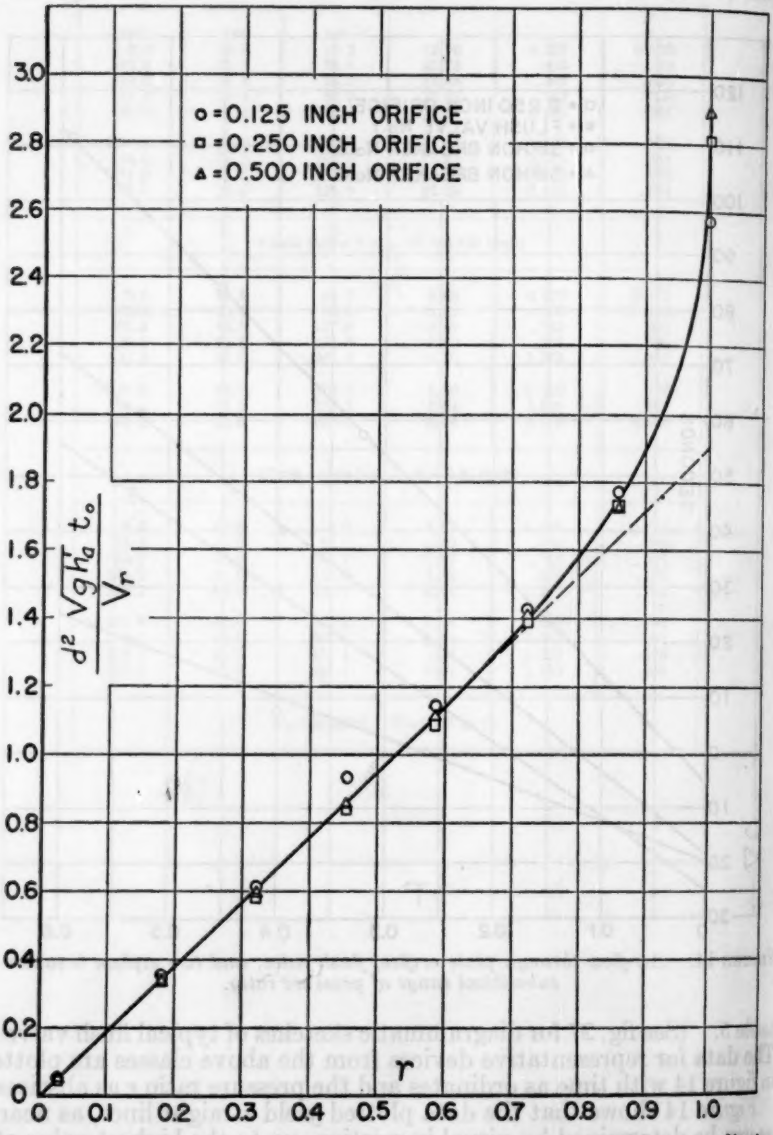

FIGURE 15.—*Air-flow curve for simple plate orifices: Dimensionless coordinates.*

By using these particular variables, the data for the three orifices were brought together in a single curve, instead of yielding three separate

curves, as would have been the case had the variables t_0 and r been used, as was done in figure 14.

Before this could be done, however, it was necessary to correct the time interval t corresponding to any particular observed value of r by adding the increment Δt that would have been required to increase the pressure in the tank from absolute-zero pressure to the initial pressure P_0 that existed at the beginning of the run in question. These corrections Δt were obtained from plots similar to that shown in figure 14 by extending the straight lines to cut the axis $r=0$ and reading off the intercepts thus obtained. The time intervals to be used in plotting the following eq 26 corresponding to the observed pressure ratios r_0, r_1, r_2, etc., are then Δt, $t_1+\Delta t$, $t_2+\Delta t$, etc., respectively.

Work by earlier investigators made it appear that it would be legitimate to neglect the temperature change ΔT in eq 25 for the purposes of the present investigation; so, omitting the factor $\left(\frac{1-\Delta T}{T_a}\right)$ and writing t_0 for t, eq 25 becomes

$$r=\frac{C\pi N}{4}\times\frac{d^2\sqrt{gh'_a}}{V_r}\times t_o \tag{26}$$

Figure 15 shows the curve for the plate orifices tested with values of

$$\frac{d^2\sqrt{gh'_a}}{V_r}\times t_0$$

plotted as ordinates and values of r as abscissas. The data used in preparing this figure are given in table 2.

It will be observed that the data for the three orifices fall very closely on the same straight line over the range $0<r<r_c$. Since the coefficient C of the orifice was not taken into account in computing values of

$$\frac{d^2\sqrt{gh'_a}}{V_r}\times t_0,$$

this fact indicates that the three orifices had the same constant coefficient C over this range, within the limits of accuracy of the experiments. The points for the smallest orifice tend to deviate slightly from the straight line given by the two largest orifices, showing that the ratio of the thickness of the plate to the diameter of the orifice may have been a little too great for the smallest orifice, causing it to differ slightly from the characteristic performance of a thin-plate orifice.

(c) EQUIVALENT ORIFICES

It may be useful, especially to the manufacturers of flush valves and siphon-breakers, to make a comparison of the air-flow characteristics of these devices with the characteristics of simple plate orifices. This can be done by means of the curve for plate orifices in figure 15 and the data for siphon-breakers and valves given in tables 3, 4, and 5.

The curve of figure 15 is reproduced in figure 16. If we enter this curve with the value of r for any determination for a particular device,

such as a given siphon-breaker, within the range $r<r_c$, we may read the corresponding value of

$$\frac{d^2\sqrt{gh'_a}}{V_r}\times t_0.$$

Knowing the value of t_0 corresponding to the value of r with which we entered the curve, we may now compute the diameter d_e of a circular orifice equivalent to the orifice in the device tested. The equivalence, to be more exact, is between C_1d_1 and C_2d_2, where C_1 and d_1 are, respectively, the flow coefficient of the orifice and the diameter for the plate orifice, and C_2 and d_2 are the corresponding factors for the device, since C_1 and C_2 have not been employed in plotting the curve and probably have different values for the different devices.

Now using the value of d_e thus determined, values of

$$\frac{d^2\ \overline{gh'_a\times t_0}}{V_r}$$

can be computed for the other observations for the device and can be plotted as has been done in figure 16. It is obvious that the flush valve and the two siphon-breakers for which data are given in this figure do have the same air-flow characteristics as a simple plate orifice, so that the performance of each can be expressed in terms of the performance of a plate orifice having the equivalent diameter d_e, the value of which can be determined as explained above.

All of the siphon-breakers and flush valves tested were compared with the plate-orifice curve in figures 15 and 16, and all were found to have the same characteristics as a plate orifice. The data selected for illustration in figure 16 are for three different types of devices—one flush valve, one moving-part siphon-breaker, and one nonmoving-part siphon-breaker.

This relation just established is important, because most flush valves and some siphon-breakers have inner passages or orifices which control the maximum rate of backflow of air but which cannot be measured readily. If the performance curve for a simple plate orifice is available in the form given in figure 15, a single test on a device having such irregular orifice or one of unknown diameter will supply the data necessary for determining the diameter of a simple plate orifice that will have the same capacity.

It will be observed from figure 16 that for the irregular orifices and for the plate orifices the linear relation between r and t_0 extends to a value of r greater than 0.527. The experiments thus appear to justify the assumptions that the mass rate of flow is constant for all pressure ratios between 0 and 0.527, and that this establishes the safe limit for computing the maximum rate of flow through an opening into an evacuated water-supply system and for testing for the maximum external effects of such evacuated systems.

3. SAFE AIR GAPS

Reference has been made in the preceding section to the critical flow of air through an orifice and to the fact that the rate of flow through an opening or orifice in the critical range $0<P_r/P_a<r_c$ remains

sensibly constant throughout that range and is the maximum that can occur. In the problem of safe air gaps, we are concerned only with the maximum effects of the air-flow and may therefore restrict the problem to determining the minimum gap (fig. 17) that will preclude all

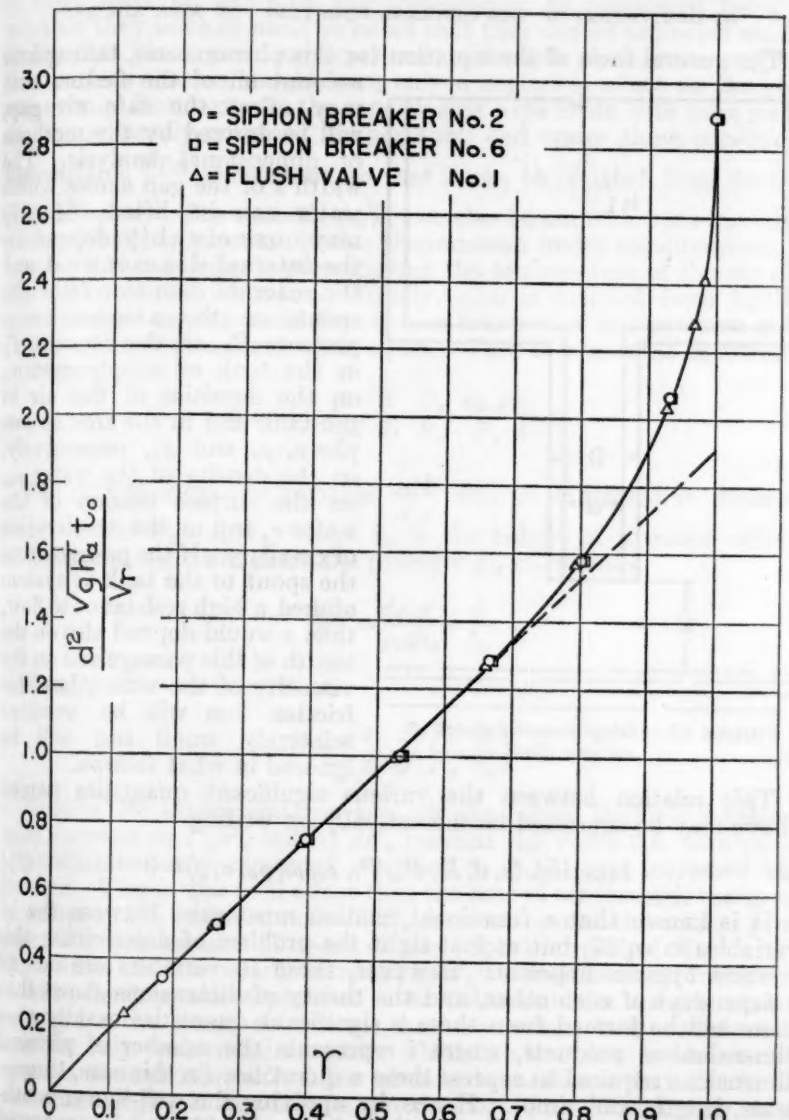

FIGURE 16.—*Air-flow curve for flush valve and siphon-breakers: Dimensionless coordinates.*

possibility of backflow of water under the most unfavorable pressure condition that can occur; that is, when there exists the maximum possible rate of air-flow across the gap. Mr. R. H. Zinkil, of the

Crane laboratories, has published the results of experiments on safe air gaps [28], and these results have been employed here in the derivation of an empirical equation for the safe air gap under any condition that may be encountered.

(a) DERIVATION OF THE GENERAL EQUATION FOR SAFE AIR GAP

The general form of the equation for this phenomenon, taking into account all of the factors that may affect the safe air gap, will be derived by the methods of dimensional analysis. The width x of the gap across which water can be lifted (fig. 17) may conceivably depend on the internal diameter d and the external diameter D of the spout, on the atmospheric pressure P_a, on the pressure P_r in the tank or supply system, on the densities of the air in the tank and in the free atmosphere, ρ_r and ρ_a, respectively, on the density of the water ρ_w, on the surface tension of the water σ, and on the acceleration of gravity g. If the passage from the spout to the tank or system offered a high resistance to flow, then x would depend also on the length of this passage and on the viscosity of the water, but this friction loss will be assumed relatively small and will be ignored in what follows.

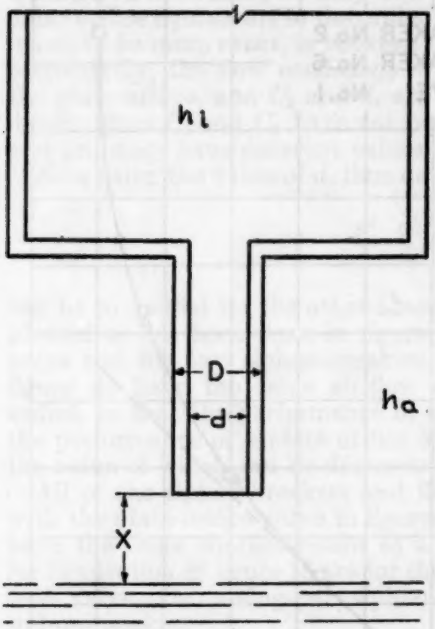

FIGURE 17.—*Diagrammatic sketch of air gap.*

This relation between the various significant quantities named above may be expressed mathematically by writing

$$\text{function } (x, d, D, P_a, P_r, \rho_a, \rho_r, \rho_w, \sigma, g)=0 \tag{27}$$

It is known that a functional relation must exist between the 10 variables in eq 27, but at first sight the problem of determining this relation appears hopeless. However, these 10 variables are not all independent of each other, and the theory of dimensions shows that there can be formed from these n significant quantities exactly $n-i$ dimensionless products, where i represents the number of physical dimensions required to express these n quantities (in this case, three—mass, length, and time). Hence, by applying the well-known methods of dimensional analysis [29] the relation (eq 27) can be expressed in the following form, involving only products and quotients of the 10 quantities, so combined as to give variables in which the physical dimensions cancel out, thus yielding a functional relation between $10-3=7$ dimensionless variables:

$$\text{function } \left(\frac{x}{d}, \frac{d}{D}, \frac{d^2\rho_w g}{\sigma}, \frac{d\rho_w g}{P_a}, \frac{\rho_w}{\rho_a}, \frac{\rho_r}{\rho_a}\right)=0 \tag{28}$$

The function has thus been simplified by reducing a relation between 10 quantities to one between 7 quantities, but further simplification is necessary if a simple, usable relation is to be found. The next step is to examine the variables in eq 28 to see whether any of them have no effect on the phenomenon as considered here, or whether they have so small an effect that they can be neglected safely. In the first place, previous experience with such phenomena suggests that surface tension should have only a negligible effect on the phenomenon. Furthermore, the experiments were made with pure water at approximately constant temperature, and under these conditions the variable $\frac{d^2\rho_w g}{\sigma}$ is constant, so that it can be omitted from further consideration. The variable ρ_w/ρ_a can also be omitted from consideration, since it is constant in the phenomenon under consideration, as long as the atmospheric pressure and the temperature of the air and the water remain constant. Finally, ρ_r/ρ_a is omitted from further consideration on the basis that it is a function of the pressure ratio P_r/P_a, which is also involved in eq 28. Thus it is possible to simplify eq 28 to

$$\text{function}\left(\frac{x}{d}, \frac{d}{D}, \frac{P_r}{P_a}, \frac{d\rho_w g}{P_a}\right)=0 \tag{29}$$

For convenience, the variable $\frac{d\rho_w g}{P_a}$ will be expressed in different form. Since $P_a=\rho_w g h_a$, where h_a is the height of a water column of density ρ_w that will exert the pressure P_a at its base,

$$\frac{d\rho_w g}{P_a}=\frac{d\rho_w g}{\rho_w g h_a}=\frac{d}{h_a},$$

and eq 29 can now be written

$$\text{function}\left(\frac{x}{d}, \frac{d}{D}, \frac{P_r}{P_a}, \frac{d}{h_a}\right)=0 \tag{30}$$

Zinkil's [28] experiments on safe air gaps show that x/d increased with decrease in P_r/P_a until P_r/P_a reached the value 0.5, to a rough approximation, and remained constant as P_r/P_a was increased still further. This is due to the fact that the flow of air through the spout increases as the pressure ratio P_r/P_a decreases, until the critical pressure ratio (see section IV-2-(a) of this paper) is reached after which the air-flow remains nearly constant as P_r/P_a decreases still further.

Since the immediate problem is to determine the air gap that is safe under the worst conditions that can occur, it is sufficient to consider only the conditions under which the backflow of air into the spout is a maximum; and it has already been shown that this is the case when P_r/P_a is less than approximately 0.5. Within this range of values of the pressure ratio, x/d has a sensibly constant maximum value. With this restriction on the value of P_r/P_a, it is no longer necessary to treat the pressure ratio as a variable, and eq 30 simplifies to

$$\text{function}\left(\frac{x}{d}, \frac{d}{D}, \frac{d}{h_a}\right)=0, \tag{31}$$

which is simple enough to be fitted to the existing data.

(b) EMPIRICAL EQUATION FOR SAFE AIR GAP

Using Zinkil's data given in table 6 for spouts with a circular cross section, the following empirical equation, which applies within the limits $0.125<d<0.806$ inch, and $0.361<d/D<0.919$, was obtained in terms of the three dimensionless variables in eq 31:

$$x/d=2.45\left(1-0.26\,\frac{d}{D}\right)\left(1-114\,\frac{d}{h_a}\right) \tag{32}$$

in which x, d, D, and h_a can all be taken in inches, in feet, in centimeters, or in any other unit of length that is desired. One advantage of using dimensionless variables is the fact that the constants in the equation remain the same when a change is made from one system of consistent units to another consistent system. If it is desired to have all these quantities in inches, then, neglecting local variations in atmospheric conditions, h_a may be taken as 408 inches head of water for standard atmospheric pressure at sea level.

This equation may be employed to compute the safe gap x for any faucet within the range of diameters given in table 6, namely, $0.127<d<0.806$ inch and $0.36<d/D<0.92$. These ranges willl include all practical faucets up to an internal diameter of 0.8 inch. However, it is desirable for purposes of construction and inspection to have the minimum permissible gap expressed in a simpler form.

TABLE 6.—*Minimum air gap for various orifices and vacua*

[Values in parenthesis obtained by extrapolation]

Orifices			Minimum air gap x for various vacua						Ratios	
Type of opening	Dimensions		Vacua in inches of mercury						d/D	x/D
	d	D	2	5	10	15	20	Over 20		
	in.	*in.*	*in.*	*in.*	*in.*	*in.*	*in.*	*in.*		
6 in. tube	0.127	0.188	0.16	0.22	0.23	0.24	0.24	0.25	0.675	1.97
Plate orifice	.127	.311	.19	.24	.26	.27	.28	.28	.408	2.20
6 in. tube	.187	.249	.23	.30	.33	.33	.34	.34	.752	1.82
Plate orifice	.187	.501	.26	.32	.36	.38	.38	.38	.374	2.02
6 in. tube	.227	.312	.28	.36	.39	.41	.41	.41	.728	1.81
Plate orifice	.227	.629	.31	.39	.42	.44	.45	.45	.361	2.04
6 in. tube	.403	.501	.50	.59	.66	.66	.66	.66	.806	1.64
Plate orifice	.403	.876	.52	.63	.69	.72	.74	.74	.461	1.84
6 in. tube	.570	.627	.65	.79	.86	.87	(.88)	(.88)	.910	(1.54)
Plate orifice	.570	1.122	.68	.82	.93	.95	(.97)	(.97)	.509	(1.70)
6 in. tube	.806	.873	.86	1.14	1.25	(1.26)	(1.26)	(1.26)	.924	(1.56)
Plate orifice	.806	1.623	.93	1.25	1.34	(1.35)	(1.36)	(1.36)	.497	(1.66)

It will be observed that in eq 32 the value of x/d is increased by decreasing either or both of the ratios d/D and d/h_a in the second member of the equation. Therefore, if a group of faucets falls within definite limits in dimensions, for example, $0.375<d<0.5$ inch and $d/D<0.5$, an approximate value for the safe gap for any faucet in the group, but slightly greater than the minimum safe gap for any particular faucet in the group, may be obtained by substituting maximum and minimum limits in eq 32 and solving it for x. Thus, if 0.5 inch is substituted for d in the ratio x/d, 0.5 for d/D, and 0.375 inch for d and 408 inches for h_a in the ratio d/h_a, the resultant equation is

$$x/0.5=2.45(1-0.26\times 0.5)\left(1-114\frac{0.375}{408}\right), \qquad (32a)$$

from which $x=0.96$ inch approximately. In this manner a safe air gap expressed as a concrete number may be obtained for any limited range in faucet sizes, and this range may be chosen to correspond to the sizes of faucets used with the different kinds of plumbing fixtures, for example, lavatory faucets, sink faucets, bathtub faucets, etc.

Data published in Zinkil's paper, but not tabulated here, indicate that, in the case of oval sections, d and D may be safely taken as the mean of the maximum and minimum diameters of the internal and external sections respectively, and that for faucets set at an angle, x may be taken safely as the mean of the maximum and minimum distances of the spout from the highest possible water surface.

It may also be pointed out that the data given in table 6 show a tendency for the ratio x/d to decrease as d increases. This signifies that a margin of safety will be given by employing eq 32 to compute the safe gap for faucets or other supply outlets larger than 0.8 inch in mean internal diameter.

4. SIPHON-BREAKERS

The principle of siphon-breakers presents another special case of the flow of air through orifices. A siphon-breaker, using the term broadly, includes any device for the prevention of backflow of water through a water-supply branch, the outlet of which is submerged, or may become submerged, under service conditions. Excepting the simple check valve, the principle on which all these devices depend in common for their effectiveness in preventing backflow, is the arrangement of two orifices in series. If a check valve is leaking, the same principle still applies.

The essentials of this arrangement of orifices are illustrated diagrammatically in figure 18. These are: an inner orifice i opening from the supply branch to the flush pipe, and an outer orifice O, opening from the flush pipe to the outer air, either orifice being a single passage or any number of separate passages. If a vacuum occurs in the supply system on which a siphon-breaker is installed, a stream of air will flow through the outer orifice into the flush pipe, then from the flush pipe through the inner orifice into the water-supply system.

The problem consists in determining the relation between the ratio of the cross sections or capacities of the two orifices and the permissible rise of water in the flush pipe (fig. 18) before it can mix with the stream of air and be carried through the inner orifice into the supply branch. The height of rise in the flush pipe will be equal to the difference in pressure Δh between the pressure in the flush pipe and the prevailing atmospheric pressure h_a; hence Δh determines the minimum value that x can have if the siphon-breaker is to be fully effective. Since the mass rate of flow through the two orifices is the same, the maximum value of Δh will occur when the mass rate of air-flow is a maximum. Also since x, the permissible rise, must be small for structural reasons, Δh must also be kept small, and therefore the outer orifice must have a capacity sufficient to hold the loss in pressure head Δh to the value of x or less when the flow through the inner orifice is a maximum; that is, when critical flow through the

inner orifice occurs. These relations are given in the paper [10] by Professor Camp previously referred to but were not analyzed in detail for all types of siphon-breakers.

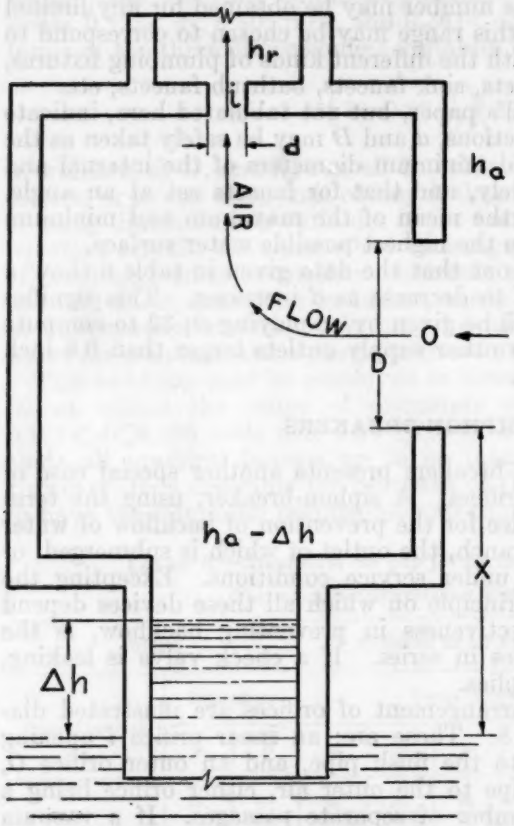

FIGURE 18.—*Diagrammatic sketch of siphon-breaker.*

(a) DEFINITION OF EFFECTIVENESS

We may define the effectiveness of any siphon-breaker as the ratio of the permissible rise of water x in the flush pipe to the maximum possible rise Δh under any vacuum that may occur, or $x/\Delta h$. If $x/\Delta h \geqq 1$, the device will be effective under any pressure conditions that can occur in the water-supply system. If $x/\Delta h < 1$, the device will be ineffective under the maximum possible effects of vacuum but may be effective for the conditions that actually occur in particular systems. It may be pointed out that, for any pressure conditions, the margin of safety of the device can be increased either by increasing x, the height it is placed above the water level in the fixture (permissible rise), or by decreasing Δh, the minimum limit of effectiveness, which can be accomplished by increasing the capacity of the outer orifice relative to the capacity of the inner orifice.

(b) DETERMINATION OF EFFECTIVENESS

If the dimensions of the inner and outer orifices of a siphon-breaker are known, so that the ratio of the cross-sectional areas or of the diameters d and D of equivalent circular openings can be determined, it is possible to compute approximately the effectiveness of the device. For this purpose, Δh can be expressed in terms of the diameter ratio d/D by considering the flow through the inner and outer orifices separately. (See fig. 18.) It will be assumed that the value of the pressure ratio

$$P_r/P_i = \frac{h_r}{h_a - \Delta h}$$

for the inner orifice is less than the critical value, $r_c = 0.527$; and, since Δh is very small in comparison with h_a, it will be ignored, so

that the pressure ratio for the inner orifice will be taken as $P_r/P_a = h_r/h_a$.

The following equations then apply to the inner orifice, under the assumption that the flow is adiabatic:

$$m=\frac{C_i\pi d^2}{4}\rho_c v_c,\ v_c=\left(\frac{P_c k}{\rho_c}\right)^{1/2},\ \frac{\rho_c}{\rho_a}=\left(\frac{P_c}{P_a}\right)^{1/k},\ \text{and}\ P_c/P_a=r=0.527$$

where C_i is the flow coefficient for the inner orifice, and the other quantities have already been defined.

Since the pressure drop across the outer orifice will be very small, of the order of one inch of water, it will be assumed that the flow through the outer orifice is isothermal, in order to simplify the computation. The following equations then apply to the outer orifice:

$$v_0=(2g\Delta h')^{1/2},\ \text{and}\ Q=\frac{m}{\rho_a}=C_0\frac{\pi D^2}{4}v_0,$$

where C_0 is the flow coefficient of the outer orifice, Q is the volume rate of flow, and $\Delta h'$ is the drop across the outer orifice expressed in height of an air column of standard density ρ_a. Utilizing the fact that the mass rate of flow must be the same for both orifices, the following equation can be derived from the equations given above:

$$\Delta h=1/2h_a\times r^{\frac{k+1}{k}}\times k\times\left(\frac{C_i}{C_0}\right)^2\left(\frac{d}{D}\right)^4. \tag{33}$$

If the value 408 inches of water is substituted for h_a, 0.527 for r, and 1.4 for k, eq 33 becomes

$$\Delta h=95.2\left(\frac{C_i}{C_0}\right)^2\left(\frac{d}{D}\right)^4\ \text{(inches of water)}. \tag{33a}$$

Furthermore, if we take the maximum value of unity for C_i and an average value of 0.60 for C_0, i. e., $C_i/C_0=1.67$, then

$$\Delta h=265\ (d/D)^4\text{(inches of water)}. \tag{33b}$$

Values of Δh from eq 33a are plotted against d/D in figure 19 for three values of the ratio C_iC_0; 1.5, 1.75, and 2.0. If the diameter ratio d/D and the value of x are known for the siphon-breaker in question, it is possible to use eq 33a or a plot similar to figure 19, using the proper value of C_i/C_0, to determine the value of Δh.

Conversely, in the design of a siphon-breaker, if the equivalent diameter of the inner orifice is known, the equivalent diameter of the outer orifice that will keep Δh within any desired limit can be determined.

In general, the orifices in siphon-breakers and flush valves will not be simple circular openings. However, as a first approximation, the value of d or D, as the case may be, can be based on a circular area equal to the measured cross-sectional area of the irregularly shaped openings. In case the orifices are circular and are accessible, the diameters d and D can be measured directly. A reason for believing that this procedure is legitimate is the fact that, as figure 16 shows, the devices tested behaved exactly as if the orifices in them were simple circular openings, although actually in some cases they were very irregular and consisted of several parallel small passages.

(c) TYPES OF SIPHON-BREAKERS

Commercial siphon-breakers designed for the prevention of backflow into water-supply branches may be classified into two comprehensive groups: (1) Moving-part siphon-breakers, and (2) nonmoving-part siphon-breakers.

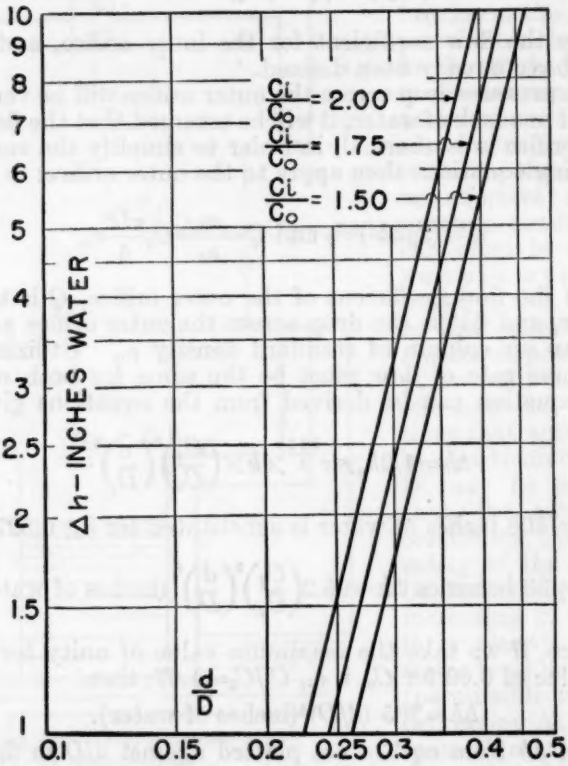

FIGURE 19.—*Rise of water level in flush pipe as a function of the ratio of the diameters of the inner and outer orifices.*

(d) MOVING-PART SIPHON-BREAKERS

Two forms of moving-part siphon-breakers are shown in figures 20 and 21, each of which is designed for insertion in the flush pipe between a flush valve and water closet or other plumbing fixture. The types shown consist of a check valve, through or around which a small opening (inner orifice) is provided, and of a larger opening (outer orifice) from the flush pipe to the outer air. Another suggested form,[4] in which the moving part consists of a single disk and loose-fitting guide, is illustrated in figure 22 and may be constructed in the offset

[4] Since the design for a siphon-breaker of the type illustrated in figure 22 was completed, a sample of one constructed on almost the same pattern has been submitted to the National Bureau of Standards for examination. Another siphon-breaker employing the same principle, but constructed in a form suitable for installation in the supply branch on the supply side of a valve or faucet, was submitted for examination in January 1936, prior to starting this investigation. Therefore, the authors make no claim of originality or priority in developing the principle in a form suitable for use in the flush pipes of flush valves.

form as shown, or in a symmetrical form, giving it an external appearance similar to figure 21.

In operation of the types shown in figures 20, 21, and 22, and others employing the same principle, the check valve remains closed in the protective position when water is not flowing through the device. When the flush valve is tripped, starting the flow of water through the

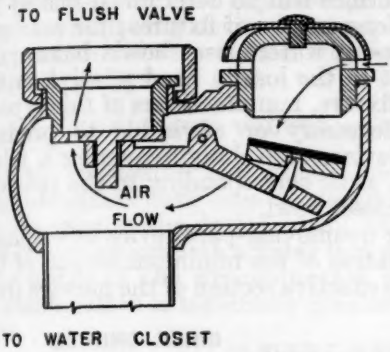

FIGURE 20.—*Moving part.*

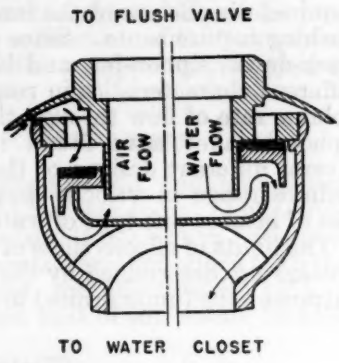

FIGURE 21.—*Moving part.*

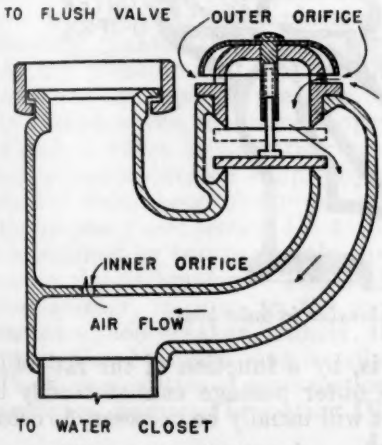

FIGURE 22.—*Moving part.*

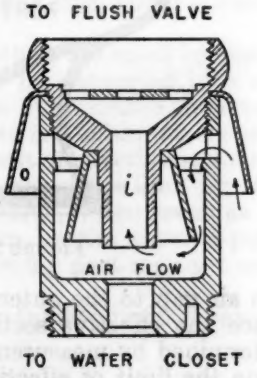

FIGURE 23.—*Nonmoving part.*

FIGURES 20–23.—*Types of siphon-breakers.*

device, the check valve opens, simultaneously closing the outer orifice to prevent an outflow of water through it, and again drops into the protective position when the water stops flowing, the moving part thus being forced through its complete cycle of motion with each flush of the fixture.

(e) NONMOVING-PART SIPHON-BREAKERS

Figure 23 illustrates the essentials of a nonmoving-part siphon-breaker, commonly referred to as the venturi type. It consists of an entrance tube tapering to a minimum section (inner orifice) *i*, an exit tube enlarging from a section slightly larger than the minimum section of the entrance tube to the same as that of the flush pipe, a

definite air gap between the entrance and exit tubes, and an enclosed passage (outer orifice) O, between the air gap and outer air.

In order to function satisfactorily as a part of the flushing mechanism, the device must pass water under the available service pressure at the volume rate or rates required to flush the fixture satisfactorily and deliver the water to the fixture with a velocity head equal to or greater than the loss in head through the fixture, and therefore the required dimensions of the inner orifice will be determined mainly by flushing requirements. Since different types of fixtures; for example, wash-down, siphon-jet, and blow-out water-closet bowls have quite different characteristics in respect to the loss in head relative to the volume rate of flow through the fixture, manufacturers of this type of siphon-breaker have found it necessary or advisable to produce several different designs of the device, each design covering a fairly definite range in velocity heads, each corresponding to the range in loss of head in one type of water-closet bowl.

The limits of effectiveness of the nonmoving-part device as a siphon-breaker are determined by the relation of the minimum section of the entrance tube (inner orifice) to the effective section of the passage from

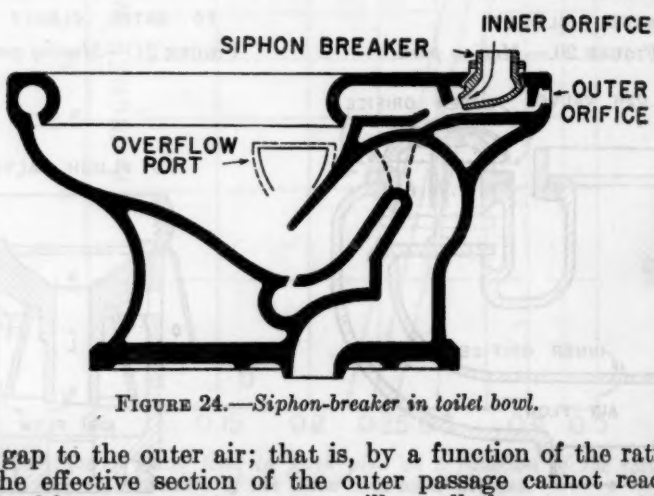

FIGURE 24.—*Siphon-breaker in toilet bowl.*

the air gap to the outer air; that is, by a function of the ratio d/D. Since the effective section of the outer passage cannot readily be determined by measurement, a test will usually be necessary to determine the limit of effectiveness $x/\Delta h$.

One manufacturer has installed a siphon-breaker of the nonmoving-part type in the flush chamber of the water-closet bowl (fig. 24). The principle involved is exactly the same as that already described, except that the closet bowl is also provided with an overflow below the rim ports which in effect gives two siphon-breakers in series, thereby increasing the over-all effectiveness. It may be pointed out in this connection, however, that, so long as the bowl is not clogged and the rim ports are open, there will be two siphon-breakers in series in any outfit in which a siphon-breaker is installed in the flushing mechanism of a jet-action water closet.

There are also adjustable nonmoving-part siphon-breakers being offered which are intended for application to any type of water-closet bowl. As none of these adjustable nonmoving-part devices has been examined in connection with this investigation, and since the authors

have no record of their use in actual service, no conclusions as to their serviceability can be drawn here.

There is one other feature of nonmoving-part siphon-breakers to which attention may be called at this time. They all depend on an increase in the velocity of flow through an open gap in order to give the necessary velocity head for flushing the fixture and to reduce the pressure in the gap to atmospheric pressure in order to prevent the flow of water from the gap through the outer orifice. The noise produced by a flushing device is principally a function of the velocity of flow, and therefore a siphon-breaker of the nonmoving-part type is inherently noisy.

5. FLUSH VALVES AS SIPHON-BREAKERS

In the preceding paragraphs, moving-part and nonmoving-part siphon-breakers have been discussed from the standpoint of effectiveness inherent in the device itself. Obviously, if the siphon-breaker is used in connection with a valve that presents a smaller orifice than the inner orifice of the siphon-breaker proper, the effectiveness $x/\Delta h$ of the combination is materially greater than that of the siphon-breaker alone.

(a) STABLE FLUSH VALVES

Some flush valves are stable under a vacuum. By a "stable flush valve" is meant one which closes automatically under a line pressure sufficiently greater than atmospheric pressure and remains closed under any pressure that may occur in the supply line, either greater or less than atmospheric pressure.

In a stable valve, the passage open to backflow is the small by-pass, and such a valve in operating condition can be converted into an effective siphon-breaker simply by giving it an outer orifice the cross section of which bears the proper relationship to the minimum section of the by-pass f (see section IV–4–(b)). The limit of effectiveness may be determined by test in exactly the same manner as the limit for the separate siphon-breaker. The stable flush valve, when used as a siphon-breaker, is open to the same criticism as the moving-part detached siphon-breaker, namely, that the moving part may get out of order, thereby destroying its effectiveness.

The characteristics of construction on which stability in flush valves depends are discussed in section IV–7–(c).

(b) SIPHON-BREAKERS INTEGRAL WITH FLUSH VALVES

There are two types of construction in which the siphon-breaker may be said to be integral with a flush valve; one in which the siphon-breaker is constructed in the flush chamber of the valve body and functions independently of the valve mechanism proper, and the other in which the valve mechanism is utilized as a part of the siphon-breaker. The principle of the former does not differ from that of the detachable siphon-breaker except that the characteristics of the particular valve may be taken into account in determining its over-all effectiveness. The latter type is applicable only to the so-called stable valve.

It should be pointed out that, in installing any siphon-breaker, the minimum projected elevation x of the lower of the two orifices above

the highest possible level of water in the fixture should not be less than the highest possible value of Δh as determined from the dimensions of the orifices or by test.

6. TESTS FOR EFFECTIVENESS

(a) APPARATUS REQUIRED

In most cases the effective diameters or areas of the orifices of siphon-breakers cannot be determined readily by measurement of dimensions, and in these cases a test will be necessary to determine the limit of effectiveness $x/\Delta h$. Figure 25 shows the essential parts of the equipment for making a test for effectiveness. The apparatus shown consists of: (a) A vacuum tank; (b) a vacuum pump; (c) a gage or manometer for measuring the pressure in the vacuum tank; (d) a water manometer or sensitive gage for measuring the pressure drop Δh in the flush pipe below the device being tested; (e) fittings for mounting the device and closing the flush pipe of the device; and (f) the siphon-breaker under test. The piping between the

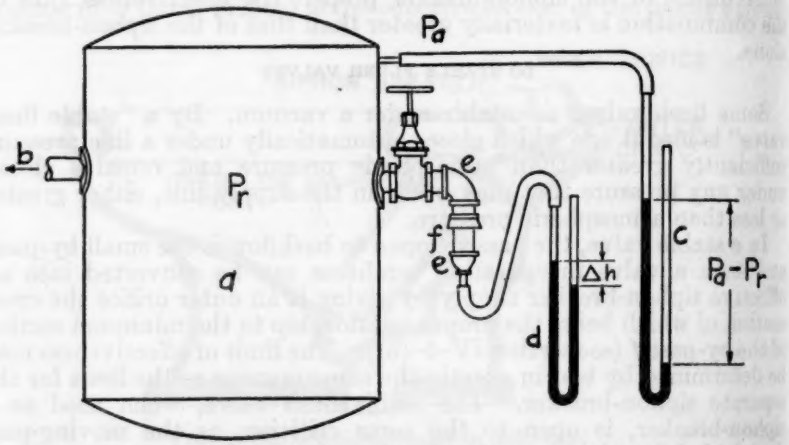

FIGURE 25.—*Sketch showing essential parts of apparatus for testing siphon-breakers.*

device and the vacuum tank should be short, and not smaller in diameter than the nominal size of the connection for which the device is designed. Figure 26 is a photograph of the equipment as used for these tests.

(b) ESSENTIALS FOR AN ADEQUATE TEST

A device can be tested adequately simply by evacuating the tank to a degree sufficient to maintain critical flow through the inner orifice for a long enough time to obtain a reading of the maximum drop in pressure Δh indicated on the gage *d*. For an atmospheric pressure of 30 inches of mercury, this means a pressure $P_r < 0.527\, P_a = 15.8$ inches of mercury in the tank or a mercury manometer reading (gage *c*) of $(30 - P_r) > 14.2$ inches of mercury. All connections, especially manometer and gage connections, should be tight.

The test for effectiveness described is for the limit of effectiveness inherent in the device itself. The limit of effectiveness of a siphon-breaker in combination with a flush valve and water closet may be quite different. If the passage through the flush valve is smaller

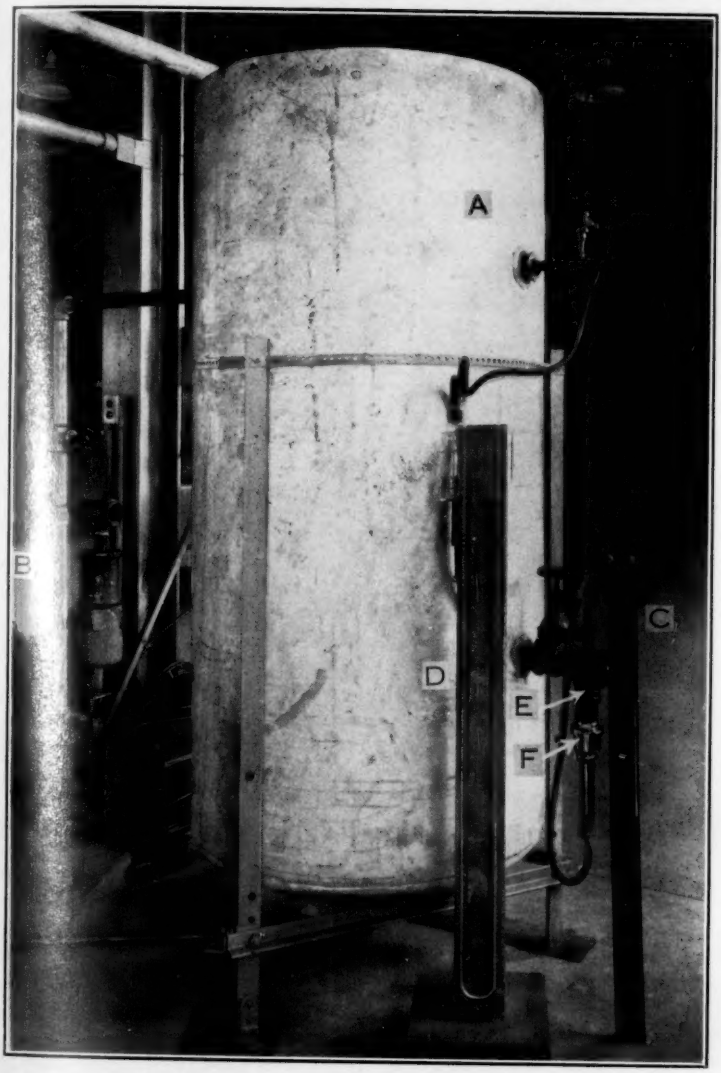

FIGURE 26.—*Apparatus used in air-flow tests.*

than the inner orifice of the siphon-breaker, the flush valve and not the inner orifice controls the rate of flow, and the effectiveness of the siphon-breaker in combination with this valve is increased. Hence the siphon-breaker may be set lower and still be fully effective. If the rim ports of the closet bowl are not submerged, they act as additional orifices, and the over-all effectiveness of the combination is increased. It is impossible to determine the magnitude of the effects of flush valves and closet bowls on the limit of effectiveness except in connection with specific valves and specific bowls, and then only by a test for over-all effectiveness. It follows that the inherent effectiveness of a siphon-breaker is the only basis on which limits can be set for universal application with all flush valves and all water-closet bowls.

(c) CAPACITY OF TEST EQUIPMENT

There has been considerable discussion among those interested in the prevention of backsiphonage as to what equipment is required for making a conclusive test of the effectiveness of a siphon-breaker. The required capacity of the tank depends on the size of opening through the device to be tested, the minimum pressure to which the tank can be evacuated, the types of instruments employed for making the necessary observations, on the adeptness of the testing personnel in manipulating the apparatus, and on the capacity of the pump, in case the test is made with the pump running. It will be found much more economical to install a tank adequate to meet the capacity requirements independently of the capacity of the vacuum pump, as the cost of high-vacuum pumps increases rapidly with increase in capacity. The essential requirement for a test of a siphon-breaker to determine its limit of effectiveness for use in any water-supply system; that is, for use in any or all water-supply sustems, and with any and all types of flush valves, is that critical flow through the device shall be maintained long enough to make the necessary readings or observations for determining the limit of effectiveness.

Assuming that a vacuum pump or other means is available for evacuating the tank to a known degree, for example, to a pressure of 2 inches of mercury (28-in. mercury vacuum), the time given for making observations may be estimated. The time required to change the pressure in the tank from P_r=0.067 atmosphere (=2 in. of mercury or 2.25 ft of water), to P_r=0.527 atmosphere (=15.8 in. of mercury or 17.9 ft of water), will be roughly (depending on the character of the opening) from 2 to 2.5 seconds per 100 gallons of tank capacity for an opening (orifice) in the device 1 inch in diameter; from 8 to 10 seconds through an opening ½ inch in diameter; and from 32 to 40 seconds through an opening ¼ inch in diameter. Assuming the same initial degree of evacuation, the time available for taking the necessary observations will vary directly as the volume of tank and (roughly) inversely as the square of the diameter of the orifice.

In the test of a nonmoving-part siphon-breaker with a ¾-inch diameter inner passage, the pressure P_e in the 318-gallon tank (fig. 26) increased from 0.26 atmosphere to 0.527 atmosphere in 7.5 seconds, and a simple computation shows that, if the initial tank pressure had been 0.067 atmosphere, it would then have taken about 13 seconds for the

tank pressure to increase to 0.527 atmosphere. This is equivalent to about 4 seconds per 100 gallons capacity of the tank, a value which is in fair agreement with the estimate made above.

7. STABLE AND UNSTABLE FLUSH VALVES

(a) DEFINITION OF STABLE AND UNSTABLE VALVES

There are certain characteristics in the performance of automatic flush valves, under a reversal of pressure differential, that have a direct bearing on the practical application of the principles of siphon-breakers to these valves. A *stable flush valve* has been defined as one which closes automatically under a pressure in the supply line sufficiently greater than the atmospheric pressure and remains closed under any pressure in the supply line, either greater or less than atmospheric pressure, this last condition constituting a reversal of the pressure differential. An *unstable flush valve* will be defined as one which closes automatically under a pressure in the supply line sufficiently greater than the atmospheric pressure, but which opens under a pressure in the supply line appreciably less than atmospheric pressure. In any case, for either opening or closing, the difference between the line pressure and atmospheric pressure must be sufficient to supply the force necessary to overcome the combined frictional and gravitational forces opposing the movement of the valve.

(b) OPERATION OF FLUSH VALVE UNDER NORMAL PRESSURE CONDITIONS

It will be necessary to discuss the general principles of operation of automatic flush valves in order to explain the principles of stability. However, although there are many types and forms of flush valves in use in plumbing installations, it will be sufficient for the purposes of this paper to describe and discuss two types in detail—the piston and the diaphragm types.

A piston valve is shown diagrammatically in figure 27 in the closed and in the open positions, and a diaphragm valve is shown similarly in figure 28. These valves consist essentially of the valve body a; a piston or diaphragm b, which constitutes the moving part of the main valve; a pressure chamber c; a flush chamber d; an auxiliary release valve e; a by-pass f, connecting the pressure chamber to the line pressure; and a handle g for setting the valve in operation. When the valve is closed, the service-line pressure P_1 acts on the annular area A_1 on the under side of the piston or diaphragm, giving a force P_1A_1 upward. The pressure P_2 in the pressure chamber c acts on the area A_2 on the top of the piston or diaphragm, giving a force P_2A_2 downward. The pressure P_3 in the flush chamber d acts on the central area of the piston or diaphragm A_3, giving a force of P_3A_3 upward. The resultant force F on the piston or diaphragm is given then by the relation

$$F=P_2A_2-P_1A_1-P_3A_3+W, \tag{34}$$

in which W is the weight of the piston or diaphragm assembly and forces acting downward are taken as positive. Neglecting friction, the valve will then seat and remain seated, provided F is positive. When the valve is closed under a service pressure P_1 sufficient to operate the valve, $P_2=P_1>P_3$, and eq 34 becomes

$$F=(P_1-P_3)A_3+W, \tag{35}$$

since $A_2=A_1+A_3$ exactly for the piston-type valve and approximately for the diaphragm-type valve. Since P_1-P_3 under any operating service pressure is always positive, F will always be positive under these conditions.

When the auxiliary valve is tripped to open the main valve, the pressure P_2 becomes sensibly equal to P_3 temporarily, and eq 34 becomes

$$F=(P_3-P_1)A_1+W, \tag{36}$$

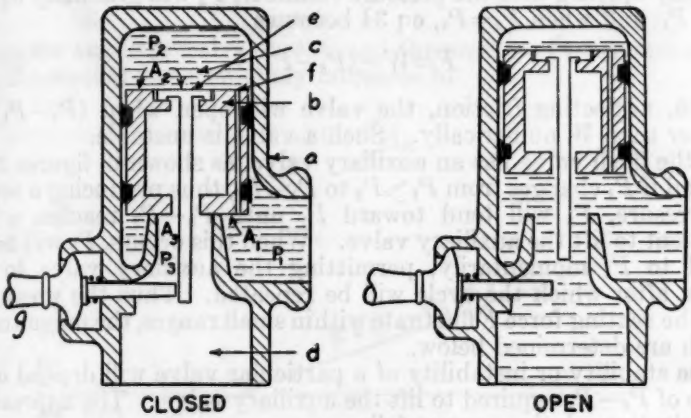

FIGURE 27.—*Piston-type flush valve.*

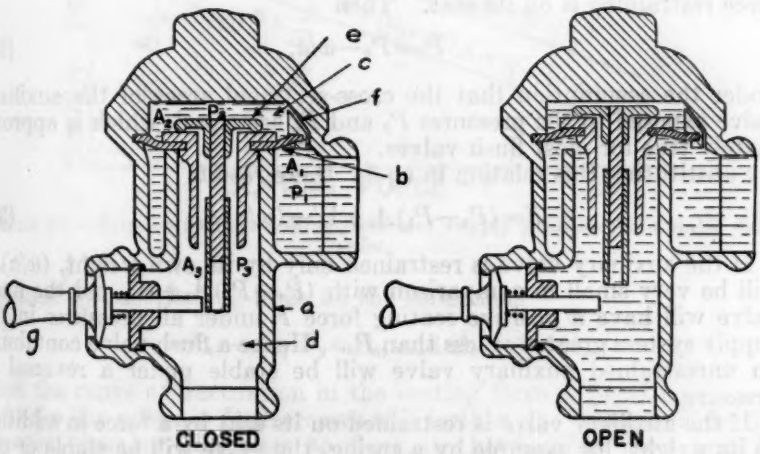

FIGURE 28.—*Diaphragm-type flush valve.*

and since P_3-P_1 is negative, the valve will open, provided $(P_3-P_1)A_1$ is numerically greater than W, as it is in any actual valve.

Once the pressures P_2 and P_3 have equalized, the auxiliary valve seats once more, the pressure P_2 starts to equalize with the line pressure P_1, and the main valve seats as soon as the value of F, as given by

eq 34, becomes positive. The timing of the valve depends on the size of the by-pass and the volume of the pressure chamber, either or both of which may be adjustable.

(c) CONDITIONS FOR STABILITY OF FLUSH VALVES

Whether a flush valve will remain closed or will open under a subatmospheric pressure in the water-supply system, i. e., when $P_1 < P_3 = P_a$, depends on whether the value of F in eq 34 remains positive or becomes negative under these pressure conditions. If the by-pass is the only opening into the pressure chamber, P_2 will gradually equalize with P_1, and when $P_2 = P_1$, eq 34 becomes

$$F = W - (P_3 - P_1)A_3. \tag{35}$$

Hence, neglecting friction, the valve will open when $(P_3 - P_1)A_3$ is greater than W numerically. Such a valve is unstable.

If the flush valve has an auxiliary valve, as shown in figures 27 and 28, and if P_1 changes from $P_1 > P_3$ to $P_1 < P_3$, thus producing a reversal of pressure, P_2 will tend toward P_1 until $P_3 - P_2$ reaches a value sufficient to lift the auxiliary valve. When this occurs, P_2 will become equal to P_3 momentarily, permitting the auxiliary valve to close again, after which the cycle will be repeated. Thus the pressure P_2 and the seating force F fluctuate within small ranges, the magnitudes of which are determined below.

The stability or instability of a particular valve will depend on the value of $P_3 - P_2$ required to lift the auxiliary valve. The approximate quantitative relations are as follows:

Let a = the cross-sectional area of the auxiliary valve and w = the force restraining it on its seat. Then

$$P_2 = P_3 - w/a, \tag{37}$$

under the assumption that the cross-sectional areas of the auxiliary valve exposed to the pressures P_2 and P_3 are equal, which is approximately true for most flush valves.

Substituting this relation in eq 34 there results

$$F = (P_3 - P_1)A_1 + W - (w/a)A_2. \tag{38}$$

If the auxiliary valve is restrained only by its own weight, $(w/a)A_2$ will be very small in comparison with $(P_3 - P_1)A_1 + W$, and the main valve will have a positive seating force F under all pressures in the supply system greater or less than P_3. Hence a flush valve containing an unrestrained auxiliary valve will be stable under a reversal of pressure.

If the auxiliary valve is restrained on its seat by a force in addition to its weight, for example by a spring, the valve will be stable or unstable under a reversal of pressure according to whether $(w/a)A_2$ is less or greater than $(P_3 - P_1)A_1 + W$. If the total restraining force w is small compared to W, the valve will be stable. If w is large compared to W, it will be unstable.

Figure 29 illustrates the relation of the seating force F to the pressure P_1 for a stable piston-type flush valve for reversal in pressure from $P_1 > P_3$ to $P_1 < P_3$.

Referring to figure 29, if we assume that the valve is closed and has been closed long enough for P_2 to equalize with P_1, then eq 35 repre-

sents the relation between the seating force F and the line pressure P_1 for all values of P_1 greater than P_3-w/a, which is the pressure at which the auxiliary valve will unseat. (See eq 37.) The value of the seating force corresponding to this value of P_1 is obtained by substituting in eq 34 the conditions

$$P_1=P_2=P_3-w/a, \text{ and } A_2=A_1+A_3,$$

and proves to be

$$F=W-\frac{w}{a}A_3.$$

When the auxiliary valve unseats and the pressure P_2 becomes equal to P_3, the seating force suddenly increases to

$$F=W+\frac{w}{a}A_1,$$

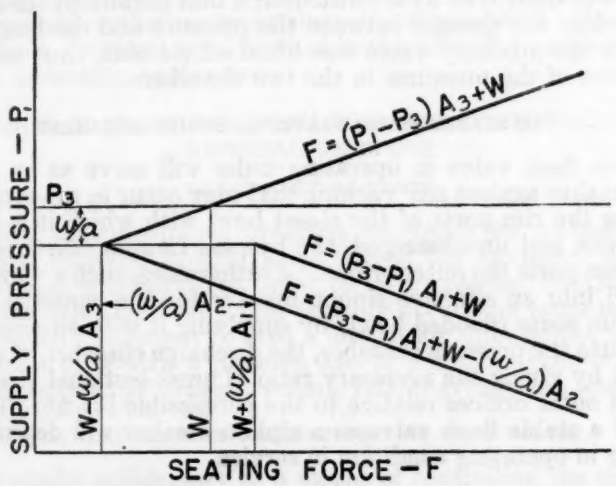

FIGURE 29.—*Relation between seating force and supply pressure for a stable flush valve.*

obtained by substituting in eq 34 the conditions

$$P_1=P_3-w/a,\ P_2=P_3, \text{ and } A_2=A_1+A_3.$$

Thus the range of fluctuation in the seating force is $(w/a)A_2$.

As the line pressure P_1 decreases still further, the pressure P_2 in the pressure chamber continues to fluctuate between P_3-w/a and P_3 because of the repeated unseating and seating of the auxiliary valve, and the seating force continues to increase, fluctuating over a range $(w/a)A_2$ continuously. Thus, for values of P_1 less than P_3-w/a, the seating force is represented by a band lying between two parallel lines, in which the seating force is always positive. The equations of these two bounding lines can be obtained by substituting the proper values of P_2 in eq 34.

It may be concluded from the preceding analysis that the stability of flush valves when subjected to subatmospheric pressures in the supply system depends on the pressure in the pressure chamber being held to slight variations below atmospheric pressure by an unrestrained or slightly restrained auxiliary valve or by a vent from the pressure chamber to the outer air, the latter combined with a check valve, if used.

Numerical values for the pressures and the areas used in the preceding discussion can be assigned only for particular valves. However, it is obvious that many flush valves would still remain stable if some slight restraint is applied to the auxiliary valve.

A number of different flush valves were examined to investigate their stability under a reversal of pressure gradient by measuring the areas A_1, A_2, and A_3 and by testing the valves under various vacua. With one exception, all the valves of the fully automatic type, in which the motion of the auxiliary valve was unrestrained by a spring, were stable, as the term is defined in this paper. In this one exception, the stability was destroyed by a construction that permitted the auxiliary valve to close the passage between the pressure and discharge chambers when the auxiliary valve was lifted off its seat, thus preventing equalization of the pressures in the two chambers.

(d) STABLE FLUSH VALVES AS SIPHON-BREAKERS

A stable flush valve in operating order will serve as an effective siphon-breaker against any vacuum that may occur in the supply lines as long as the rim ports of the closet bowl with which it is installed remain open and unsubmerged, the by-pass forming the inner orifice and the rim ports the outer orifice. Furthermore, such a valve can be converted into an effective siphon-breaker for the condition of submerged rim ports (flooded bowl) by supplying it with an outer orifice opening into the pressure chamber, the discharge chamber, or the flush pipe, and by giving the necessary ratio of cross-sectional areas of the inner and outer orifices relative to the permissible lift Δh. The reliability of a stable flush valve as a siphon-breaker will depend on its remaining in operating condition in service.

V. PREVENTION OF BACKFLOW IN WATER-SUPPLY SYSTEMS

Two possible methods of preventing backflow through potential cross-connections in water-supply systems are suggested by the preceding analysis of conditions (section III) and by the effects of vacua in plumbing systems (section IV): (1) The prevention of a pressure drop in the water-supply system sufficient to produce a pressure differential in any supply branch in the direction of the supply system, and (2) the prevention of siphon action in any supply branch, assuming that any possible vacuum may exist in the water-supply system.

Protection by the first method would have to be accomplished by certain forms of construction in respect to sizes and arrangement of supply pipes and by venting to control the pressure in the system to a definite minimum limit, which limit in each case will depend on the shortest down-feed supply branch of the system. Obviously, the capacity of the vents required to hold the pressure in an evacuating water-supply system above a definite minimum limit will depend on

the volume rate of evacuation and not directly on the total or final volume evacuated. Since no definite limit can be set for the rate of evacuation that will occur in particular water-supply systems, in order to be on the safe side, it will be necessary to assume that the rate in a particular system may be the maximum that can occur in any vertical system, thus depending on the terminal velocity of flow in a vertical pipe of the diameter of the main supply pipe in the particular system (see section IV–1).

The second of these methods will be applied through the form of construction in the supply branch to the fixture (safe air gap) and by the use of special devices (siphon-breakers) in supply branches. Since there are no definite limits that can be set for the evacuated volume and minimum pressure that will occur in particular unvented water-supply systems short of the total internal volume of the system and the limiting vacuum pressure h_e, and since the maximum effects of a vacuum in producing backflow occur when the flow of air through the supply branch is a maximum, it will be necessary to proceed on the assumption that the evacuated volume and the pressure in any system may be sufficient to produce these maximum effects. The two methods of control are discussed in the following paragraphs with reference to specific application.

1. PREVENTION OF BACKFLOW BY FORMS OF CONSTRUCTION AND GENERAL VENTING

(a) CAPACITY OF VENTS

Assuming that down-feed branches are employed exclusively in a system and that the vertical projection of the minimum down-feed supply branch is x inches, in order to insure against backflow under any service condition that might possibly occur, the vents must have a total capacity sufficient to give a flow of air through the vents and piping equal to Q with a pressure loss of not more than x inches of water, where Q is the terminal volume rate of evacuation (see table 1).

(b) PERFORMANCE REQUIREMENT OF VENT VALVES

To be wholly satisfactory as a means of controlling the pressure in up-feed systems within a definite minimum limit, a vent or relief valve should have the following performance characteristics: (1) It should open fully and positively under a small drop in pressure (not more than x inches of water) below atmospheric pressure in order to prevent an initially low pressure from developing in the system; (2) it should close positively and remain closed at or slightly below atmospheric pressure in order to prevent outflow of water through the vent valve; and (3) these operations should be dependable after long periods of inactivity under service pressure. Until a valve having these performance characteristics has been developed and its dependability under all conditions has been determined, prevention of backflow in up-feed water-supply systems will not be in general a feasible method. However, the method of control by general venting can be applied to simple down-feed water-supply systems.

The essentials of construction for complete protection against backflow into a simple down-feed water-supply system (see fig. 2) are: (1) An overhead supply tank open to atmospheric pressure; (2) a continuous down-feed system through the main supply pipe (riser)

from the tank and all branches in which there is any possibility of cross-connection with fixtures; (3) a separate supply branch from the riser to each fixture or an arrangement within any multiple branch, such that a siphon cannot be created within the branch; (4) a proportioning of the riser and branches in such a manner that the friction loss in head under maximum service demands will not reduce the pressure at the connection of any branch to the riser to less than (h_a-x) inches of water, where h_a is the atmospheric pressure in inches of water, and x is the vertical projection of the branch in inches; and (5) the use of open-top fixtures where any cross-connection with the water-supply system is possible. If the main supply riser from the tank has a shut-off valve as shown in figure 2, then in addition the system must have a vent pipe connected below the shut-off valve and extending above the water level in the supply tank as indicated. This method is feasible for a simple down-feed system, and can be made effective for any down-feed system. However, in a complicated down-feed system with a supply header and several risers, the method, although possible, would probably prove impractical on account of the extensive venting costs necessary to meet the requirements. It would be difficult also for building officials to determine whether the construction in particular buildings meets these requirements or not. It would seem from these considerations that, for the present at least, a general and practical control of conditions will be restricted to the second method of attack.

2. PREVENTION OF BACKFLOW IN SUPPLY BRANCHES

Assuming no provision for controlling the minimum pressure that may occur in water-supply systems, there are three ways in which backflow into the system can be restricted or prevented: (1) By safe air gaps; (2) by siphon-breakers; and (3) by check valves.

(a) SAFE AIR GAP

In open-top plumbing fixtures that do not require a direct connection from the water-supply system, the obvious and economical means of preventing backflow is to provide a safe air gap,

$$x=2.45\,d\left(1-0.26\,\frac{d}{D}\right)\left(1-0.28\,\frac{d}{h_a}\right)\text{ (see eq 32),}$$

between the supply opening (faucet spout) and the highest possible level to which water can rise in the fixture or receptacle. Also a safe air gap slightly larger than the minimum may be specified as a concrete number applicable to a limited range of sizes of faucets or supply outlets, for example, $x=a$ inches (see eq 32a and discussion). This method may be used effectively in any cross-connection where a direct connection is not essential for the proper functioning of the fixture.

(b) SIPHON-BREAKERS

Where a clear air gap between the fixture and the water-supply branch is impractical, for example, in water-closet bowls with flush-valve supply, a siphon-breaker can be installed to prevent backflow. The effectiveness of such a device is measured by $x/\Delta h$,

where x is the vertical projection from the lowest orifice in the siphon-breaker to the highest possible water level in the fixture, and Δh is its effective limit. A value of $x/\Delta h=1$ signifies full effectiveness inherent in the device itself, and the margin of safety increases with the value of this ratio.

There has been considerable rivalry in the past between the advocates of the two general types of siphon-breakers (moving-part and nonmoving-part) and some controversy regarding their relative merits. Questions of this nature can be answered best by stating the general characteristics of the two types for consideration in regard to their effectiveness in preventing backflow, dependability, and general serviceability. For each pattern or design of either type there is a definite minimum limit to the distance x which the device may be set above the top of a water-closet bowl and give 100 percent effectiveness in preventing backflow.

The nonmoving-part siphon-breaker must be suited in design to the flushing characteristics of the closet bowl with which it is installed, and it is impossible to design a single model, without an adjustment feature, suitable for use with water-closet bowls distinctly different in their flushing characteristics or to design a single model, whether adjustable or not, that will be completely effective in preventing backflow when x is small. There is no assurance that a siphon-breaker suitable for the closet bowl at the time of installation will be suitable later if the flushing characteristics of the closet bowl change after a period of service. Also the nonmoving-part siphon-breaker is inherently noisy in operation.

The design of a moving-part siphon-breaker is not dependent on the characteristics of the water-closet bowl, so it can be designed to make it completely effective for very low values of x and quiet in operation.

Objections to the moving-part siphon-breaker have been made on the grounds that the moving part may get out of order in service and cease to function and that it does not permit a rapid relief of vacua in water-supply systems. Whether the former objection is a valid one or not can probably be most convincingly answered by the history of these devices in actual service. In reference to the latter objection, it may be pointed out that there is no logical reason for relieving the vacuum in a water-supply system if all supply outlets from the system are protected against backflow. Also it will be a distinct service disadvantage if the water-supply system is permitted to fill with air every time a subatmospheric pressure occurs, since the air has to be let out before the system can refill.

(c) PREVENTION OF BACKFLOW BY CHECK VALVES

A check valve alone can not be regarded as positive protection against backflow through a cross-connection, because of possible failure to operate. However, in any existing direct cross-connection, it may be less hazardous to permit the use of a check valve or combination of check valves than to remove the cross-connection, if its removal would introduce a different hazard or increase one already existing, as, for example, the fire hazard. Control of such conditions is more a matter of judgment, based on a knowledge of the local conditions, such as pressure variations, nature of the cross-

connection, character of the waters in the two systems, etc., than of facts of general analysis. The only certain way to prevent flow through a direct cross-connection is to remove the cross-connection or convert it into one that can be controlled positively.

(d) PROTECTION OF CLOSED FIXTURES

Since there is no means of determining the maximum back-pressure which a closed fixture may exert on a direct supply connection, there is no apparent means of positively preventing backflow through a cross-connection of this type. If the direct supply connection is essential, the only certain way of preventing pollution of the main water supply of the building is by means of a separate or auxiliary water-distributing system to fixtures of this type. If the direct-supply connection is not essential for satisfactory service, then the obvious way of preventing backflow is to convert the cross-connection to one in which a safe air gap may be employed.

(e) AUXILIARY SUPPLY SYSTEMS

An auxiliary water-distributing system for water closets and urinals has been advocated and used to some extent as a means of preventing contamination of the main water supply. If such an auxiliary system has no connection or branch through which water might be drawn for drinking or domestic purposes, and if the main system is fully protected against backflow from the auxiliary system by a safe air gap between the two, the method is perfectly safe, so long as the system remains unaltered by structural changes. Objections to this method of protecting the main water supply are principally on the basis of cost, and on the assumption that the system may be altered without the knowledge or consent of the health authorities. However, in some cases, the cost of installing an auxiliary supply system may not exceed the cost of installing siphon-breakers for individual fixtures, and it is impossible to estimate or weigh the chance of unauthorized alterations.

3. COMBINATION OF METHODS OF PREVENTING BACKFLOW

There is, of course, the possibility of combining the method of general venting with the use of siphon-breakers on the supply branches for a limited number of fixtures. It has been suggested that siphon-breakers or vacuum-breakers may be constructed to serve the functions of venting, thereby preventing low-pressure vacua from occurring in the water-supply system. There are, however, difficulties in applying this method effectively that are practically insurmountable at the present stage of development. First, the siphon-breakers of large venting capacity so far developed are suitable for use only on the fixture side of the supply control valve, and therefore the rate of inflow of air into the supply system (venting) will depend principally on the valve and not on the siphon-breaker or vacuum-breaker. In the case of compression faucets and stable flush valves, the venting through the valve will in general be negligible in its effects, since these valves ordinarily are closed. In the case of unstable flush valves, the maximum inflow of air into the supply system, though much greater than through the by-pass of a stable valve under the same pressure conditions, will still be a function of the valve rather

than of the siphon-breaker. Furthermore, if a siphon-breaker wholly satisfactory for use on the supply side of the flush valve has been or can be developed, it might just as readily be installed on the top of risers and principal supply branches, where it would be most effective in controlling the pressure in the system. Finally, if all supply outlets are fully protected by air gaps or by siphon-breakers, there is no need for controlling the pressure in the water-supply system.

VI. PRACTICAL CONSIDERATIONS IN THE APPLICATION OF RESULTS

The ultimate purpose of this investigation is to supply information on which to base effective health regulations pertaining to the installation of plumbing. Presumably these regulations, when they become law, will be mandatory and will affect many different groups—the owners or managers of properties, the public officials charged with the enforcement of the regulations, architects, sanitary engineers, manufacturers of plumbing materials, contractors (master plumbers), workmen (journeymen plumbers), and the public who occupy or use the buildings and who use the public water supply.

There have been apparently two widely different or extreme attitudes toward the hazard created by cross-connections in plumbing systems: (1) The attitude or viewpoint that a distinct hazard exists wherever there is any possibility of backflow into the water-supply system, however remote; and (2) the attitude that the hazard offered by an indirect (potential) cross-connection in a plumbing system is negligible because the combination of conditions necessary to complete the cross-connection is not likely to occur in most plumbing installations. Between these two extreme views, any number of opinions as to the seriousness of the hazard and as to specific necessary corrective measures, as well as noncommittal attitudes, may be encountered among those who have given the problem some thought. Therefore, it is to be expected that these differences in opinion and attitudes cannot be wholly reconciled without further and possibly prolonged discussion of the subject.

The analysis of the problem in the preceding sections of this paper, as has been stated frequently, has been developed from the standpoint of complete protection against backflow under the most extreme conditions, not because this is necessarily the correct basis from the standpoint of the most satisfactory or most effective health regulation, but because it is the only basis on which definite limits and definite performance specifications for corrective measures can be established. In fact, in spite of the extreme attitude that may appear to be supported by this discussion as a whole, the authors are of the opinion that a conservative attitude on the part of those who may be called upon to formulate either recommended or mandatory regulations for the prevention of backflow in plumbing systems will result in a more effective control than an intolerant attitude which demands immediate perfection.

Because of the varied interests affected, it would appear that if possible, the interested parties should be satisfied that any regulations which may be adopted are reasonable in their requirements and are necessary for the protection of the health of the public. It would

also appear that these varied groups should have, through competent representatives, a voice in the formulation of the proposed regulations, in order that the viewpoint of each particular group may be presented and considered. For these reasons, this paper deals principally with the technical phases of the problem, and no attempt has been made to draw final conclusions as to the form or scope of the regulations that may be based on the information given. From the standpoint of the practical application of the results, the investigation is incomplete, and the major part of the investigation, in some respects the most difficult part, is yet to be accomplished.

The committee or organization that may be called upon to formulate a satisfactory regulation, and the legislative body to which this proposed regulation may be presented for enactment into law, will be confronted not only with the technical problems dealt with in this paper but also with the social and economic problems of obtaining compliance with the law after its enactment. The effectiveness of any health regulation that may be adopted will be determined by the degree of obedience to it rather than by its literal requirements. It will therefore be advisable in formulating the law to consider very carefully the probable results of the law from the standpoint of enforcement or obedience. In this connection the following questions may well be raised and carefully considered:

1. Will a mandatory health regulation aimed at a complete prevention of backflow into the water-supply system in any building under any possible condition that may occur prove as effective in its results as a regulation less exacting in its scope of application and in the completeness of the protection given?
2. Should the mandatory regulation apply only to new construction, or should it be retroactive and apply to all plumbing, with the attendant difficulties of surveys, condemnation, and enforcement of replacements in existing structures?
3. Should the regulation apply equally to all types of buildings, public and private, or should some limit of mandatory application be set, as, for example, to hospitals, hotels, restaurants, and other buildings of a similarly public character?
4. Should any differentiation be made in the mandatory application of the regulation in reference to topography, zoning, etc.? Or should a differentiation be made in respect to the type of cross-connection?

These are some of the questions that may well be raised in advance of the formulation and enactment of any mandatory regulation. Any regulation that appears unreasonable in its requirements will invite evasion and violation of the law, thus to a large extent defeating its real purpose.

It may be worth while to illustrate some of the difficulties referred to in the preceding paragraph. For example, the minimum air gap that will give complete protection against backflow from an open-top faucet-supplied plumbing fixture under any pressure condition that can occur is roughly 1.8 d, where d is the mean internal diameter of the faucet nozzle. This is based on the simultaneous occurrence of a sustained vacuum pressure of less than 0.527 atmosphere in the supply line, a fixture filled to the rim, and an open faucet. Obviously, this combination of conditions will occur only infrequently in any system and will never occur in some systems. Obviously, too, any clear air

gap, however small, will give protection in any system the greater part of the time, regardless of the maximum vacuum and maximum flooding of fixtures that may occur at irregular and infrequent intervals. Again, there is no possible way of determining whether the conditions that are necessary to produce backflow from a particular fixture having an air gap less than 1.8 d will or will not occur in an up-feed water-supply system of a particular building, and therefore, there is no possible way of determining what air gap less than 1.8 d would suffice to give complete protection to a particular fixture on a particular system.

The situation in regard to other types of cross-connections is similar; and, because of this situation, attempts to classify cross-connections as to the relative danger of backflow become a matter of judgment or opinion and not one of scientific fact. It may become necessary, however, to make a classification of cross-connections on the basis of the menace to health offered by them in order to reduce or to restrict the field of mandatory application to one that can be adequately handled and controlled. Fortunately, when corrective measures are necessary for protection, either by special forms of construction or by the use of special devices, it will usually be as easy and as economical in new construction to obtain complete protection against backflow under any possible condition as to obtain a less complete or partial protection.

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QUICK-DRYING STAMP-PAD INKS

By C. E. Waters

ABSTRACT

Inks for use with rubber stamps are generally made by dissolving dyes in a mixture of glycerol and water. They will not dry on the pad, because glycerol is practically nonvolatile at ordinary temperatures. When an impression is made on paper, the ink "dries" by being absorbed. If the paper is absorbent, the ink may penetrate rapidly enough, but on well-sized paper it may take many seconds, or even a few minutes, for the ink to be absorbed. If many papers must be stamped in quick succession, the danger is incurred of blurring the impressions. Alcohol is one of a number of volatile organic liquids that can be added to ink made with glycerol and water, to make it sink rapidly into paper. Alcohol has the drawback of being much more volatile than water, and if ink containing it is put on a stamp-pad, much of the alcohol may be expected to evaporate soon, and the ink will no longer be quick-drying.

It has been found that Butyl Carbitol, the monobutyl ether of diethylene glycol, is not only as efficient as alcohol for making glycerol-water ink sink rapidly into paper, but it is so slowly volatile that a pad can be exposed to the air for weeks, yet the ink will still be absorbed quickly.

Most of the inks intended for use with rubber stamps are solutions of dyes in a solvent that will not dry on the pad on which the stamp is inked. The solvent is generally a mixture of glycerol and water, because glycerol, in addition to being practically nonvolatile at ordinary temperatures, is hygroscopic and never becomes completely dehydrated under atmospheric conditions.

Ink made with glycerol and water changes in fluidity according to the relative humidity of the atmosphere. It is a common complaint that it becomes watery in summer, when the air is apt to be highly humid. It does not seem to occur to many users of rubber stamps that the simple expedient of closing the lid of the box which holds the pad would be some protection against the absorption of an excessive amount of water. In cold weather, in heated buildings, the relative humidity of the air is low, and then the ink loses a large part of its water.

It thus happens that impressions made with the ink on paper dry slowly at all seasons: in summer, because the stamp takes from the pad such a large quantity of the watery ink that it takes a long time to sink into paper, for there is little or no evaporation of water from it; in winter, because the relatively concentrated and viscous ink does not readily sink into paper. If many papers must be stamped in quick succession and the ink dries slowly, the impressions may be made unsightly, or even illegible, by smearing. This state of affairs has created a demand for quick-drying inks.

There are various formulas for stamping inks made with oils, instead of with glycerol and water. They dry rapidly by being absorbed by the paper, but they can be used safely only with metal stamps, on account of the harmful effect of oils upon rubber. There are also formulas which require the use of alcohol or of ethyl acetate in a mixture of glycerol and water. Alcohol and ethyl acetate are much more volatile than water, but their rapid evaporation plays only a minor part in the drying of impressions made on paper. If a drop of water is put on a piece of good writing paper, it sinks in slowly. If a drop of alcohol, of ethyl acetate, or of several other organic liquids that might be used in ink, is put on the paper, it is absorbed almost instantly, spreads, and shows as a wet spot on the opposite side of the paper. If successive small portions of one of these liquids, for instance alcohol, are added to a mixture of glycerol and water, which contains dissolved dye, a point will be reached at which absorption by paper is rapid. If impressions are made on paper, there will be a narrow range within which the only marked effect of adding more alcohol is to increase the rate of drying by absorption. Beyond this range, with more and more alcohol, the impressions lose their sharpness, and may become blurred to illegibility. The amount of alcohol that must be used to noticeably increase the rate of drying, or that can be added without causing blurred impressions, depends greatly upon the paper. It was observed repeatedly when testing the stamp-pad inks described in this paper, as well as the recording inks discussed in an earlier paper,[1] that there was somewhat more feathering on the bond paper used by this and other Government Bureaus for letters than there was on ordinary scratch-pad paper.

Ottley [2] patented a mixture of organic liquids to be added to commercial inks to make them dry quickly. Some of the liquids have boiling points below, and some above, that of water. Although the patent says that all the liquids are "rapidly and completely volatile," more stress is laid upon the fact that the mixture "is therefore seen to be a penetrant, i. e., an agent promoting penetration."

In a later patent, Miner and Sayler [3] tell how to make writing ink sink into paper rapidly, by adding caustic soda to it. To prevent feathering on paper, small amounts of starch, of wilkinite, which is a variety of bentonite, and of ethyl xanthate are added.

So far has has been discovered, no stamp-pad ink made quick-drying by the addition of a "penetrant" that has a rather high boiling point has heretofore been described.

When spread on a stamp-pad, ink containing alcohol, ethyl acetate, or other similar liquid may be expected to become less and less quick-drying because of the evaporation of the volatile solvent. In the attempt to find a liquid that has the desirable penetrative properties of alcohol and is less volatile, two ethers of diethylene gylcol were tested. These were the monoethyl ether, commonly known as "Carbitol", and the monobutyl ether, "Butyl Carbitol." Carbitol boils at about 202° C, and Butyl Carbitol at 231° C, both at 760-mm pressure. These temperatures are in strong contrast with 78° C, the approximate boiling point of 95-percent ethyl alcohol, but they are lower than the

[1] C. E. Waters. *Inks for recording instruments*, J. Research NBS 17, 651–5 (1936) RP935.
[2] George B. Ottley. U. S. Patent 1,897,071, issued Feb. 14, 1933, for "quick-drying ink."
[3] Carl S. Miner and Galen H. Sayler. U. S. Patent 1,932,248, issued Oct. 24, 1933, for "permanent quick drying writing fluid."

boiling point of glycerol, 290° C. It was already known that neither of the ethers could be used without glycerol, because of excessive blurring, but it seemed desirable to find out how they would behave when mixed with glycerol and water, and exposed freely to the air. Accordingly, the following liquids were tested:

1. A mixture of equal volumes of glycerol and water.
2. The same as 1, with one-third its volume of Carbitol.
3. The same as 1, with one-third its volume of Butyl Carbitol.
4. Carbitol.
5. Butyl Carbitol.

Two-gram portions of these liquids were put in glass crystallizing dishes of about 48 mm inside diameter. In a dish of this size, if the bottom were perfectly flat and there were no meniscus, 2 g of water would make a layer 1.1 mm deep. The five liquids would make layers of depths slightly different from 1.1 mm. A 2-g sample of any of the liquids is enough to show definite changes in weight, and in a layer about 1 mm deep it responds more quickly to variations in atmospheric humidity than if it is in a deeper layer.

The first series of tests was started August 9, and was discontinued September 29, a period of 51 days. There was a steady loss in weight of all the liquids, except when the relative humidity was very high. The mixture of glycerol and water lost 772 of the 930 mg of water it contained at the start. Butyl Carbitol is hygroscopic, but it is also volatile, and the 2 g lost 224 mg. Because of its volatility, the mixture of glycerol and water to which it was added lost a total of 833 mg. The Carbitol lost 773 mg, and its mixture with glycerol and water, 914 mg.

A second series of tests was made in the same way as before, with the following liquids:

1. A mixture of equal volumes of glycerol and water.
2. The same as 1, with one-fourth its volume of Butyl Carbitol.
3. The same as 1, with one-fourth its volume of 95-percent ethyl alcohol.
4. Ink made by dissolving the dye fuchsine in the same mixture as 2.
5. A commercial ink made with glycerol, and containing ethyl acetate.

This series of tests was continued for 14 days, during most of which time the indoor air was very dry, so all the liquids lost most of the water they contained at the start. The mixture to which ethyl alcohol had been added and the commercial ink lost their volatile solvents, which would have occurred even with high relative humidity.

During the 2 weeks, the glycerol and water lost 882 mg, or about 95 percent of the water the mixture contained originally. The residue would almost have met the requirement of the United States Pharmacopoeia, that glycerol shall contain about 96 percent of the anhydrous substance. Liquids 2 and 4, of which Butyl Carbitol comprised one-fifth the volume, lost 812 and 809 mg, respectively. The alcohol mixture lost 1,055 mg. The viscosity of the commercial ink had already led to the suspicion that it contained more glycerol than 4, the laboratory ink, and its loss of 840 mg may be explained on this basis. The combined weights of water and ethyl acetate in the commercial ink might have been less than the combined weights of water and Butyl Carbitol in the laboratory ink, yet the commercial ink could

have shown the greater loss, on account of the low volatility of Butyl Carbitol.

In order to find out how the laboratory ink and the commercial ink behaved on pads, the same volume of each was applied to pieces of blotting paper, 44 by 50 mm. Impressions were made with a rubber dating stamp nearly every day for 19 days, on Government letter paper (25 percent rag bond) and on scratch-pad paper. With few exceptions, the impressions made with the laboratory ink were not smeared when rubbed immediately with the tips of the fingers. By the same test the commercial ink was sometimes not dry half a minute or more after the impressions were made.

The composition of the laboratory ink was decided upon after a series of tests had been made with inks prepared by adding increasing amounts of Butyl Carbitol to a solution of dye in a mixture of equal volumes of glycerol and water. Small pads of felt were inked, and impressions were made from them for a month. When 1 volume of Butyl Carbitol was added to 5 volumes of the dye solution, the impressions made with the ink dried rapidly, and when the proportion of dye solution was reduced to 3 volumes, there was no excessive feathering of the impressions. The laboratory ink, with 1 volume of Butyl Carbitol and 4 volumes of dye solution, is midway between these two. It has been given a practical trial in different offices in the Bureau, including the Mail and Files Room, where thousands of letters are stamped every month. The first pad was put in that room September 22, was reinked some time in November, and again early in January. During most of that time the lid of the box which holds the pad was not closed.

The ink is conveniently made by dissolving dye in the mixture of equal volumes of glycerol and water, filtering the solution if necessary, and adding to it one-fourth its volume of Butyl Carbitol. Before the final mixing, there is apt to be some evidence of precipitation of dye at the boundary between the glycerol-water and the Butyl Carbitol. For this reason it seems advisable in general to make the ink in the way outlined, instead of dissolving the dye in the mixture of the three liquids.

To make 1 liter of ink, there will be required 400 ml each of glycerol and water, and 200 ml of Butyl Carbitol. When the first two are mixed, the total volume is a little less than 800 ml, and there is no doubt a further contraction when the third liquid is added. The total contraction is probably overcompensated by the volume of the dye. The weight of dye to be used depends largely upon its color strength. Some dyes that have made inks of satisfactory depth of color when used in the amounts stated, per liter, are listed here. Their Colour Index numbers are given for better identification.

Dye name	Colour Index No.	Grams per liter
Fuchsine (magenta)	677	16
Light green *SF*	670	32
Methyl cotton blue	706	24
Crystal violet	681	16
Nigrosine	865	48

For those who might wish to make the ink in quantity, say by the gallon, it is pointed out that 8 g in 1 liter is equivalent to 1.0688 avdp oz/gal. All the weights of dye in the table are whole multiples of 8, so the amount of each dye required for 1 gal of ink can be found with little trouble. The concentrated forms of the dyes should be used. It is a common practice to mix colorless diluents with dyes before they are sold, so each new lot of dye bought should be tested to find out whether it has satisfactory color strength. If not, more of it must be used in a given volume of solvent.

A newly inked pad will sometimes dry out so much in the first day or two that it must be given more ink, but after this there is usually no trouble experienced with it. For use indoors in winter, when the relative humidity of the air is low, it might be advantageous to make the ink with a mixture of 2 volumes of glycerol and 1 of water. In this case the proportion of Butyl Carbitol should be increased to one-third the volume of the solution of dye, so that the finished ink will still contain 1 volume of Butyl Carbitol and 2 volumes of glycerol. Ink so made might be too hygroscopic for use in summer.

Because the ink dries almost entirely by being absorbed, the rubber stamp should not be inked too heavily, especially if the characters are large, with heavy lines, and if the stamping is done on thin paper. As already remarked, the ink dries somewhat slowly on some kinds of paper. It dries rapidly on most of the letters received by this Bureau, and this led to an unexpected result. When using the old, slow-drying ink, it was possible to stamp three or four letters with one inking of the rubber stamp. The new ink is taken up so rapidly by paper that the stamp must be inked more frequently. The chief fault so far seen is that heavily inked impressions are apt to show on the reverse of the sheet.

WASHINGTON, February 8, 1938.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1088

Part of Journal of Research of the National Bureau of Standards, Volume 20, April 1938

WATER AS A REFERENCE STANDARD FOR EBULLIOMETRY

By Wojciech Świętosławski[1] and Edgar Reynolds Smith

ABSTRACT

The properties of water are discussed with reference to its suitability as a primary standard for comparative ebulliometric measurements. The influence of small natural or accidental differences in isotopic composition with respect to the oxygen as well as to the hydrogen isotopes is shown to be negligible. The equation of Beattie and Blaisdell is suitable for obtaining the boiling point of water to 0.001° C or better at any pressure between 660 and 860 mm, and an equation, based on the data of the same authors, is given for obtaining the pressure in an apparatus from the measurement of boiling point.

The establishment of a universally recognized primary reference standard for ebulliometric investigations is necessary because comparative measurements of boiling points and condensation temperatures of liquids can be made with high precision. Numerous measurements made during recent years have demonstrated that modern ebullioscopic methods easily permit the attainment of a precision of the order of magnitude of 0.001° C in relative boiling point or condensation temperature. These methods also permit the measurement of pressure in a closed system with a relative precision of about 0.03 mm of mercury. However, such precision can be obtained with ease only by the use of comparative measurements, which require that the value determined be related directly to that of the standard reference substance. For reasons to be discussed, it appears that water is the only liquid substance possessing the characteristic properties required of a primary reference standard for such measurements, and the desirability of its adoption has been the subject of a report presented to the Committee for Physico-Chemical Data of the International Union of Chemistry.[2]

The ebullioscopic constant of water is exceptionally small, so that a content of even several thousandths percent of electrolyte has a very small effect on the boiling point. For example, the addition of 0.006 percent of sodium chloride increases the boiling point by only 0.001° C, although the electrical conductivity of such a solution is considerably increased over that of pure water. Because of this circumstance, the substances that water extracts from the walls of the container have, in practice, insignificant influence on its boiling point.

[1] Professor of Physical Chemistry at the Polytechnic Institute of Warsaw, President of the Committee for Physico-Chemical Data of the International Union of Chemistry, Minister of Education for Poland.

[2] W. Świętosławski. Comptes Rendus de la XII Conférence de l'Union Internationale de Chimie, p. 89. (1936).

Measurements, as well as theoretical considerations, demonstrate that the presence of isotopes of hydrogen and oxygen in ordinary water does not have a measurable influence on its boiling point. The boiling points of dilute aqueous solutions of deuterium water [3] in the range from 0.3 to 7 mole percent of D_2O have been shown to increase linearly with increase in D_2O, according to the equation

$$\text{Mole percent } D_2O = 70.9\,\Delta T,$$

where ΔT is the boiling point in degrees centigrade minus 100. It is obvious from the equation that an increase of 0.071 mole percent in the content of deuterium water, corresponding to an increase in density of 74 ppm, is required for an increase of 0.001° C in boiling point. No such concentration of D_2O has been found in any water from natural sources. Fluctuations in the isotopic composition of ordinary surface water from different sources and the slight fractionation which occurs during purification by simple distillation may cause differences in the boiling point of the order of 0.00005° C, which at present certainly may be neglected when using water as the primary standard for precise ebulliometric measurements.

The effect of small differences in the isotopic composition of oxygen was tested experimentally in the following way. Water having a density of 438 ppm greater than normal, prepared by electrolysis, was normalized [4] with respect to the hydrogen isotopes. The remaining difference in density was 19 ppm, due to an increase in the proportion of the heavy isotopes of oxygen, this excess being about three times as much as corresponds to the difference in atomic weight of oxygen from air and from ordinary water. A series of measurements of the differences between the boiling point and condensation temperature of this water in a differential ebulliometer of standardized dimensions,[5] as well as of the differences between its boiling point and that of normal water in a second ebulliometer, gave values always less than 0.001° C, measured with a platinum resistance thermometer. Thus the influence of naturally occurring or of small artificial differences in isotopic composition of water with respect to the oxygen isotopes, as well as to the hydrogen isotopes, is negligible.

Considering that the precision required for contemporary ebulliometric measurements is of the order of 0.001° C, water of the purity used in determinations of electric conductivity, which is readily prepared, can be regarded as suitable.

The relation between the temperature of boiling water and the pressure has been investigated a number of times by different experimenters. Ordinarily it has been customary to use the data contained in Wärmetabellen,[6] which are based on the determinations of Holborn, Scheel, Henning, Wiebe, and others. During the past 5 years, the measurements of Zmaczynski and Bonhoure [7] and of Moser [8] have also been considered excellent for comparative ebulliometric work.

[3] Edgar R. Smith and Mieczysław Wojciechowski. J. Research NBS 17, 841 (1936) RP947.
[4] Edgar R. Smith and Harry Matheson. J. Research NBS 17, 625 (1936) RP9 32.
[5] W. Świętosławski. Ebulliometry, p. 16 (Chemical Publishing Co. of New York, Inc. 1937).
[6] Wärmetabellen, (Friedr. Vieweg & Son, Braunschweig, 1919).
[7] A. Zmaczynski and A. Bonhoure. Compt. rend. 189, 1069 (1929); J. Phys. 1, 285 (1930). The results of these measurements have been recalculated recently by Zmaczynski and the figures obtained are given in table 1.
[8] H. Moser. Ann. Phys. [5] 14, 790 (1932).

More recently, however, the results of particularly careful measurements of the temperature-pressure relation for water, made with the highest accuracy attainable, have been published by two separate laboratories, the National Bureau of Standards [9] and the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology.[10] The measurements of the latter include a special study of the range 660 to 860 mm, which ordinarily is of most value for ebulliometry. The data of several investigators over this range are shown in table 1. The values of the National Bureau of Standards and the Massachusetts Institute of Technology as well as those obtained recently by Zmaczynski at the Physikalisch Technische Reichsanstalt are in agreement to better than 0.001° C. Their maximum deviation from the recalculated data of Zmaczynski and Bonhoure and from the values of Wärmetabellen over the smaller range of the latter (680 to 800 mm) is 0.002° C.

TABLE 1.—*Boiling point of water between 660 and 860 mm pressure*

Pressure	Wärmetabellen	Zmaczynski and Bonhoure [1]	Moser	Zmaczynski 1937 [2]	Osborne and Meyers	Smith, Keyes, and Gerry	Beattie and Blaisdell
mm	°C	°C	°C	°C	°C	°C	°C
660	----------	----------	----------	96.095$_5$	96.0954	96.0967	96.0964
680	96.916	96.913$_3$	96.910	96.913$_8$	96.9138	96.9144	96.9141
700	97.714	97.711$_8$	97.709	97.712$_0$	97.7125	97.7128	97.7124
720	98.494	98.491$_8$	98.490	98.493$_0$	98.4925	98.4926	98.4924
740	99.255	99.254$_2$	99.254	99.254$_4$	99.2547	99.2548	99.2546
760	100	100	100	100	100	100	100
780	100.728	100.729$_9$	100.729	100.729$_2$	100.7293	100.7292	100.7292
800	101.442	101.444$_5$	----------	101.443$_3$	101.4432	101.4431	101.4430
820	----------	102.144$_8$	----------	102.142$_3$	102.1425	102.1426	102.1424
840	----------	102.830$_4$	----------	102.827$_9$	102.8279	102.8285	102.8279
860	----------	----------	----------	103.500$_0$	103.5004	103.5017	103.5004

[1] During his work at the PTR, Zmaczynski has found the temperature coefficient of the resistance of the Smith bridge, as given by the constructor of the apparatus, to be erroneous. Since the same bridge had been used by Zmaczynski at Paris in 1929, the data obtained by him in collaboration with Bonhoure proved to be erroneous too and had to be recalculated. Zmaczynski has made these calculations now. A note with the corresponding corrections will appear shortly in the Comptes Rendus de l'Académie des Sciences.

[2] In consequence of the understanding maintained between the President of PTR, Prof. J. Stark, Charlottenburg, and Prof. W. Świętosławski, Warszawa, Drs. H. Moser and A. Zmaczynski have carried out measurements of the boiling point of water under various pressures in the limits from 270 to 2,200 mm of mercury, using two different methods. This work is not yet finished. The above table contains some of the data obtained by A. Zmaczynski by the ebulliometric method, for pressures from 660 to 860 mm of mercury.

Beattie and Blaisdell have expressed their data precisely over the range of 660 to 860 mm by the equation

$$t=100+0.0368578(p-760)-0.000020159(p-760)^2+ 0.00000001621(p-760)^3,$$

which is apparently reliable to better than 0.001° C on the International Temperature Scale for nearly 4° above and below the fixed reference point of 100° C. This precision is sufficient for every kind of comparative ebulliometric measurement, and is a potent reason for the adoption of water as a primary standard.

[9] N. S. Osborne and C. H. Meyers. J. Research NBS **13**, 1 (1934) RP 691.

[10] L. B. Smith, F. G. Keyes, and H. T. Gerry. Proc. Am. Acad. Arts Sci. **69**, 137 (1934); J. A. Beattie and B. E. Blaisdell. Proc. Am. Acad. Arts Sci. **71**, 361 (1937).

For calculations of pressure from measurements of temperature, it is more convenient to have the pressure expressed as an explicit function of the temperature. For this purpose, the original data of Beattie and Blaisdell, consisting in 4 separate runs having a total of 38 determinations of temperature and corresponding pressure between 660 and 860 mm, were treated by the method of least squares to obtain the equation

$$p=760+27.1313\ (t-100)+0.40083\ (t-100)^2+0.003192(t-100)^3$$

This equation was found to fit the MIT data with an average deviation of 0.012 mm and a greatest deviation of 0.031 mm, and to agree with the NBS data with equal precision. It may be well to point out that the equation fails rapidly above and below the range for which it was obtained.

To avoid the use of logarithms, the power series type of equation was chosen. When the use of logarithms is convenient, the following equation, suggested by N. S. Osborne and C. H. Meyers of the heat measurements section of this Bureau, is recommended.

$$\log_{10}p=5.053988-\frac{1647.6}{t+226}$$

In this equation p is expressed in standard atmospheres and t in degrees centigrade. Between 80 and 120° C, or from about ½ to 2 atmospheres, it reproduces the data tabulated by Osborne and Meyers with a precision of 0.001° C or better. In addition to validity over a greater range than the power series equation, it has the advantage of being explicit in either pressure or temperature.

In the paper by Osborne and Meyers there is given a table of the boiling point of water (table 8, condensation temperature of steam) at pressure intervals of 1 mm between 500 and 799 mm. Linear interpolation from this table is convenient, rapid, and reliable for comparative ebulliometric measurements when it is desired to avoid the use of an equation and when pressures lower than 660 mm are encountered.

When employing water as a standard, it is desirable to use a differential ebulliometer, or one having several stages [11] in order to be able, at any given moment, to compare the boiling point with the temperature of condensation of the vapor. This is of essential importance when the ebulliometer containing water is connected to another containing the liquid studied and when these two form, together with a manostat and manometer, an isolated system. This is because, in spite of all precautions, the vapors of the liquid may penetrate the ebulliometer filled with water and vice versa. By using differential ebulliometers, the purity of the water (primary standard) and of the substance studied can be verified at any time. Usually if the difference between the boiling point and temperature of condensation of the vapor does not exceed 0.001° C, contamination has not occurred to an extent which will affect the boiling point by more than a few thousandths of a degree.[12]

[11] W. Świętosławski. Ebulliometry, p. 16. (Chemical Publishing Co. of New York, Inc. (1937).)

[12] It is possible, however, that this test can fail in case of the formation of an ideal solution between two components having nearly equal boiling points. To take an extreme case, for example, the boiling point of water containing 1 mole percent of deuterium oxide is increased over that of ordinary water by 0.014° C, although the difference between the boiling point and condensation temperature is only 0.001° C.

By the use of the comparative ebulliometric method of measurement, the value of $T = T_{subst.} - T_{H_2O}$, the difference between the boiling point of the given substance and that of water boiling under the same pressure is obtained. When this difference is large, both convenience and precision would be enhanced if suitable secondary standard liquids of reliably known boiling points, covering the range of 25 to 250° C were available for the comparison. Although encouraging progress has been made,[13] the problem of establishing a series of satisfactory secondary standards for ebulliometry requires further experimental study and consideration.

WASHINGTON, January 18, 1938.

[13] W. Świętosławski. Comptes Rendus de la XII Conférence de l'Union Internationale de Chimie, p. 89 (1936).

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1089

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DETECTION OF OXIDATION IN WOOL

By Henry A. Rutherford and Milton Harris [1]

ABSTRACT

A rapid and simple test for detection of oxidation in wool is described. The method utilizes the oxidizing value of some of the intermediate oxidation derivatives of the disulfide groups in wool, and is based on the ability of oxidized wool to convert a ferrous salt into ferric salt. The latter in the presence of thiocyanate gives the characteristic red color of ferric thiocyanate.

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I. INTRODUCTION

The susceptibility of wool to deterioration during wet treatments, especially with alkaline reagents, is appreciably increased if the wool has previously been oxidized [1].[2] Damage resulting from oxidation may be produced during bleaching processes, during processes such as chlorination and bromination for producing unshrinkable finishes, and in aging conditions involving exposure to strong light, air, and moisture. Often such damage is not detectable by ordinary physical testing methods. It may, however, be accentuated during the subsequent processing of the fiber. In addition, it has been shown to affect the dyeing properties of the fiber [2] and the durability of woolen materials [3]. The detection of oxidation in wool is therefore of considerable importance.

Two tests for oxidized wool, the alkali-solubility [3] and the lead acetate tests [4], have been suggested by Smith and Harris. The former test, although somewhat time-consuming, has the advantage of giving values which have some quantitative significance, and it can be used as a control method in practical wool processes. The latter test is a qualitative one and more rapid, but it fails if the wool has been exposed to light of great intensity.

[1] Research Associates at the National Bureau of Standards, representing the American Association of Textile Chemists and Colorists. This work was aided by a grant from the Textile Foundation, Inc.

[2] Numbers in brackets indicate literature references at the end of the paper.

More recent investigations have indicated that the oxidizing value of some of the intermediate oxidation products of the disulfide groups in wool can be utilized as a test for the detection of oxidation. One method based on this fact depends on the ability of oxidized wool to liberate iodine from hydrochloric acid-potassium iodide solutions [5]. The iodine is determined by direct titration with sodium thiosulfate, but the values have no quantitative significance with respect to the extent of oxidation since only sulfur that is oxidized below the sulfonic acid state is reduced. The method was found to be impractical as a mill laboratory test since the reducing solution is unstable, the reductions must be done in the dark at a constant temperature, and the titrations are difficult because some of the liberated iodine is absorbed by the wool.

A more satisfactory test, which is described in this report, utilizes the ability of oxidized wool to convert a ferrous salt to a ferric salt, which in the presence of a thiocyanate gives the characteristic red color of ferric thiocyanate. Although the test is a qualitative one, it has the advantages of being rapid and simple, and of giving a positive test for wool which has been oxidized by photochemical reactions.

II. DESCRIPTION OF TEST

The following three solutions are required for the test.

1. Solution *A* consists of equal parts by volume of acetone (reagent-grade) and distilled water, acidified by the addition of 1 percent by volume of a 6 *N* solution of sulfuric acid. The acetone inhibits dissociation of the ferric thiocyanate and helps to preserve the color [6, 7].

2. Solution *B* is prepared by dissolving about 1 g of potassium thiocyanate in 30 ml of solution *A*.

3. Solution *C* is prepared by dissolving about 1 g of ferrous ammonium sulfate (reagent-grade) in a solution containing 50 ml of solution *A* and 15 ml of 6 *N* solution of sulfuric acid. Solution *C* must be prepared immediately before the test is made, since some of the ferrous salt is oxidized by air. The best results are obtained if the solution is prepared in an atmosphere of carbon dioxide or nitrogen.

About 1 g of wool is cut in small pieces and placed in a 125-ml Erlenmeyer flask containing 40 ml of solution *A* and 5 ml of solution *B*. The solution is boiled for several minutes to insure displacement of the air in the flask by water and acetone vapors. As soon as the heating is discontinued, 5 ml of solution *C* is added and the flask immediately stoppered. For controls, similar tests are made at the same time on a sample of wool known to be unoxidized and on the reagents in the absence of wool. A recommended procedure is to heat all of the test solutions on a hot plate at the same time.

A pink color may develop in the control solution containing only the reagents, and thus decrease the sensitivity of the test. This is overcome by the addition of a measured amount of distilled water until the color just disappears. An equal volume of water is then added to the other test solutions. Under these conditions, unoxidized wool produces no color, while oxidized wool will give various shades of pink depending upon the degree of oxidation of the sample.

The development of a pink color in the test solution prior to the addition of solution *C* indicates the presence of iron in the wool. In

such a case, the wool must first be washed with a sufficient number of changes of a very dilute solution of sulfuric acid in distilled water to remove all of the iron.

III. RESULTS

The method as described gave positive tests for wool bleached with hydrogen peroxide, for chlorinated and brominated wool, and for wool which had been exposed in the presence of air and moisture to the radiation of a glass-enclosed carbon-arc lamp. Negative tests were obtained for samples of wool irradiated in atmospheres of moist or dry nitrogen and in very dry air. Samples of wool which had been bleached with hydrogen peroxide and subsequently treated with sulfurous acid also gave negative results.

Like the reduction method, using the hydrochloric acid-potassium iodide solutions, the method should have no quantitative significance. Further evidence of this was obtained when it was found that a sample of wool which had been bleached for 2 hours with a solution containing 0.6 percent of hydrogen peroxide produced a deeper pink color in the test than was produced by a sample of wool bleached with a 1.7-per cent solution for the same length of time. In other words, the latter solution oxidized a greater number of disulfide groups to states of oxidation which resisted reduction. That the method has practical application as a qualitative test, however, is indicated by the fact that a positive test was obtained even with wool which was oxidized with a 3-percent solution of hydrogen peroxide for 24 hours. Such a treatment is far more drastic than any encountered in wool processing, yet not all of the disulfide groups were oxidized to a stage at which they resisted reduction.

IV. REFERENCES

[1] J. Research NBS **16**, 301 (1936) RP875; Am. Dyestuff Reptr. **25**, P180 (1936).
[2] J. Research NBS **19**, 81 (1937) RP1012; Am. Dyestuff Reptr. **26**, P416 (1937).
[3] J. Research NBS **17**, 577 (1936) RP928; Am. Dyestuff Reptr. **25**, P542 (1936).
[4] J. Research NBS **16**, 309 (1936) RP876; Am. Dyestuff Reptr. **25**, P183 (1936).
[5] J. Research NBS **18**, 623 (1937) RP 998; Am. Dyestuff Reptr. **26**, P413 (1937).
[6] Ind. Eng. Chem., Anal. Ed. **9**, 453 (1937).
[7] J. Biol. Chem. **1**, 451 (1906).

WASHINGTON, January 15, 1938.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1090

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REACTION OF WOOL WITH HYDROGEN PEROXIDE

By Henry A. Rutherford and Milton Harris [1]

ABSTRACT

The reaction of wool with hydrogen peroxide was investigated. The basic groups in wool are unaffected during treatment with hydrogen peroxide, as indicated by the determination of the amino nitrogen, arginine, and lysine contents. The percentage of each of the elements in wool with the exception of oxygen decreases with increased oxidation but the ratios of these elements remain constant. The results constitute further evidence that the main reaction of wool with hydrogen peroxide is the addition of oxygen to the disulfide groups.

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I. INTRODUCTION

The effect of hydrogen peroxide on wool, chiefly from the standpoint of the effect on the disulfide group, has been studied extensively by Smith and Harris [1].[2] The results of the investigations indicate that intermediate oxidation products of the disulfide group of the cystine in wool, similar to those obtained from cystine itself by Toennies and Lavine [2, 3] were formed. The latter workers isolated and studied two of these partially oxidized derivatives of cystine. Because of the lability of these compounds in acid and alkaline solutions, it was impossible to isolate any of them from the hydrolysates of oxidized wool, and as a result, the experimental evidence on which was based the postulation that partially oxidized sulfur compounds are present in oxidized wool, was of an indirect nature.

The present investigation, which is an extension of the earlier work, was undertaken to obtain more direct evidence on the nature of the effect of hydrogen peroxide on wool. The results of studies on the possibilities of oxidation of basic groups in wool are also included.

II. RESULTS AND DISCUSSION

Data which were presented in connection with a paper [4] on the nature of the acid-dyeing process showed that the acid-combining

[1] Research Associates at the National Bureau of Standards, representing the American Association of Textile Chemists and Colorists. This work was aided by a grant from the Textile Foundation, Inc.

[2] Numbers in brackets indicate literature references at the end of the paper.

capacity of wool decreased with increasing degrees of oxidation by hydrogen peroxide. Preliminary analyses of these oxidized samples also indicated that the total nitrogen content decreased with increased oxidation. These results at first suggested that an oxidative deamination was probably the cause of the decreased basicity of the samples. However, analyses of the basic groups and basic amino acids in oxidized wool did not substantiate such a mechanism. Determinations of the amino nitrogen in the different samples by the method of Rutherford, Harris, and Smith [5] showed no decrease with increasing amount of oxidation. Furthermore, the contents of arginine and lysine in the most highly oxidized sample, as determined by isolation as the flavianate [6] and picrate [7], respectively, were the same as those of a sample of the untreated wool. The complete data are given in table 1.

It is obvious that the basic groups of wool were not appreciably affected by the treatment with hydrogen peroxide, and it was therefore necessary to account in some other way for the decreases in nitrogen content and acid-combining capacity. If it is assumed that oxidation by hydrogen peroxide results in the addition of oxygen to the disulfide groups to form such compounds as R—SO—S—R, R—SO—SO—R, R—SO_2—SO—R, etc., then an answer to the apparently conflicting data in table 1 is readily found. The oxidation derivatives of the types shown are relatively strong acids and therefore decrease the amount of acid combined with the wool. Also, if oxygen has been added, there will be an increase in weight accompanied by an apparent decrease in nitrogen content.

TABLE 1.—*Effect on wool of treatment with a 3-percent solution of hydrogen peroxide at 50° C for different lengths of time*

Duration of treatment	Total nitrogen	Acid-combining capacity	Amino nitrogen	Arginine	Lysine
hr	%	M-eq/g of wool	mg/g	%	%
0[1]	16.37	0.80	3.2	7.1	1.7
3	16.24	.60	3.0	---	---
6	16.16	.53	3.2	---	---
10	15.98	.42	3.2	---	---
15	15.99	.34	3.3	---	---
20	16.04	.32	3.2	7.2	1.9

[1] Untreated.

In order to determine whether an increase in weight of the sample actually occurred during oxidation, the following experiments were made. Skeins, weighing approximately 5 g each, were placed in U-tubes and dried to constant weight in a stream of dry nitrogen at 105° C. The skeins were then treated with 200 ml of a 3-percent solution of purified hydrogen peroxide at 50° C for different lengths of time. The hydrogen peroxide used in these experiments was prepared by distillation, under reduced pressure, of a 30-percent solution of cp hydrogen peroxide, the distillate finally being diluted to 3 percent. The skeins of oxidized wool were finally washed with distilled water until the wash water was free from hydrogen peroxide. The mother liquor and wash waters of each sample were combined and evaporated nearly to dryness on a steam bath. The solutions were then transferred to weighing bottles, evaporated to dryness at

about 60° C, and finally dried to constant weight at 105° C. Microscopic examination of the residue indicated that the bulk of the material was in the form of fine fibers which had been lost during the treatment. The weights of the residues accounted for only a part of the net increases in the weights of the samples. The weights of the dry residues were added to the weights of the corresponding oxidized samples, which had been dried at 105° C in a stream of dry nitrogen. The following increases in the weight of wool samples after oxidation with a 3-percent solution of hydrogen peroxide at 50° C for different lengths of time are very appreciable and account for a large portion of the apparent decrease in nitrogen contents shown in table 1:

Duration of treatment	Increase in weight
hr	Percent
3	0. 28
6	. 90
10	1. 02
15	1. 36
20	1. 17

If the principal effect of this type of oxidation of wool is the addition of oxygen to the disulfide groups, then the percentage of each of the elements, except oxygen in wool, should decrease with increased oxidation, but the ratios of these elements in any sample should be constant. Analyses given in table 2 for the carbon, hydrogen, nitrogen, and sulfur in untreated samples and in samples oxidized for 10 and for 20 hours by the procedure previously described, show that this is so. The results constitute further evidence that the main reaction of wool with hydrogen peroxide is the addition of oxygen to the disulfide groups.

TABLE 2.—*Elementary analyses of untreated samples of wool and of samples which had been treated with a 3-percent solution of hydrogen peroxide at 50° C for 10 and for 20 hours*

Duration of treatment	Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen (by difference)	Ratio C:H:N:S
hr	%	%	%	%	%	
0[1]	50. 04	6. 92	16. 37	3. 58	23. 09	1 : 0. 138 : 0. 328 : 0. 071
10	49. 72	6. 83	15. 98	3. 45	24. 02	1 : 0. 137 : 0. 322 : 0. 069
20	49. 15	6. 80	16. 04	3. 39	24. 61	1 : 0. 138 : 0. 326 : 0. 069

[1] Untreated.

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PHOTOCHEMICAL REACTIONS OF WOOL

By Milton Harris and Arthur L. Smith [1]

ABSTRACT

In an earlier paper, the authors suggested that in the photochemical deterioration of wool, a portion of the sulfur is converted to hydrogen sulfide, some of which is subsequently oxidized to sulfuric acid. The present paper describes an apparatus which was developed for the purpose of segregating these reactions and testing the hypothesis. The results obtained with it show that in an atmosphere of purified nitrogen, hydrogen sulfide is evolved from wool during irradiation. In the presence of air the bulk of the hydrogen sulfide is oxidized to sulfuric acid. The rate of evolution of hydrogen sulfide is increased by the presence of moisture. The data suggest that the primary action of the radiation is an activation of the disulfide group, resulting in a change in the state of the sulfur. A secondary process, involving the evolution of hydrogen sulfide from the irradiated wool then occurs. Water does not appear to be essential to the process which involves changing the state of the sulfur, but it may play an important part in the secondary reactions.

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I. INTRODUCTION

In an earlier paper [1] [2], on the effect of light on wool, the authors suggested that the result of irradiation is the conversion of a portion of the sulfur to hydrogen sulfide, some of which is subsequently oxidized to sulfuric acid. In order to test this hypothesis, it was necessary to devise experiments which would segregate those reactions. The present paper describes an apparatus which was developed for this purpose. The results obtained with it are used to further elucidate the nature of some of the photochemical reactions in wool.

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[2] Numbers in brackets indicate literature references at the end of the paper.

II. DESCRIPTION OF APPARATUS AND TECHNIQUE OF OPERATION

A schematic diagram of the apparatus for exposing the wool under controlled atmospheric conditions, to the radiation of a glass-enclosed carbon arc [3] is shown in figure 1. Gases which may be evolved from the fibers are removed by carrier gases and absorbed by suitable reagents. During an exposure of a sample, the carrier gas is introduced at *A* and passes over the mercury safety valve *B*, through the trap *C*, and then through the absorption towers *D* and *E*. The latter have a capacity of about 800 ml each and are equipped with platinum disks for distributing gas similar to those described by Shepherd [2] for gas-absorption pipettes. The disks are perforated plates, each 0.05 mm thick and 20 mm in diameter, and with 212

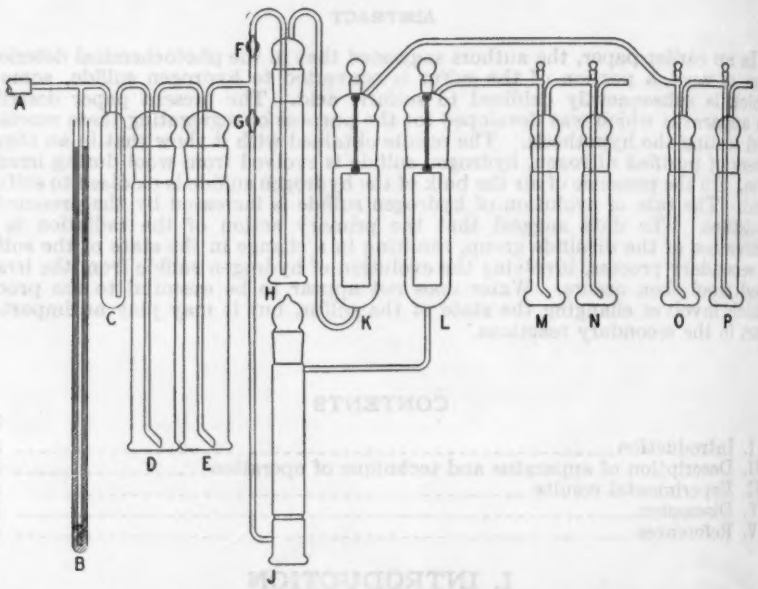

FIGURE 1.—*Schematic diagram of the apparatus for exposing wool under controlled atmospheric conditions to the radiation of a glass-enclosed carbon arc.*

evenly spaced holes, 0.06mm in diameter. When nitrogen is used as the carrier gas, *D* and *E* are filled with an alkaline solution of pyrogallol. These towers do not need to be filled when air is used. However, it was found that the presence of liquid in them facilitates the regulation of the flow of the gas. Furthermore, if a saturated solution of potassium hydroxide is used in the second tower *E*, the air is partially dried, thus permitting the material in the drying tower *J* to be used for a longer period of time. After the gas leaves *E*, it is divided into two portions, the relative amounts of each being regulated by stopcocks *F* and *G*. Part of the gas passes through *H*, which is filled with distilled water, and the remainder is dried by passing through *J*, which is filled with anhydrous magnesium per-

[3] Fade-Ometer, Atlas Electric Devices Co., Chicago, Ill.

chlorate.[4] From them the gas passes through the exposure tubes *K* and *L*, which contain the wool samples.

The gas emerging from each of the tubes *K* and *L*, finally passes through two small absorption towers *MN* and *OP*, in series. These towers have a capacity of 250 ml each and are constructed the same as the larger ones, *D* and *E*. In addition, they are fitted with ground-glass stoppers on the intake tubes to facilitate washing of the inside of the platinum distributors. Since each gas was determined in a

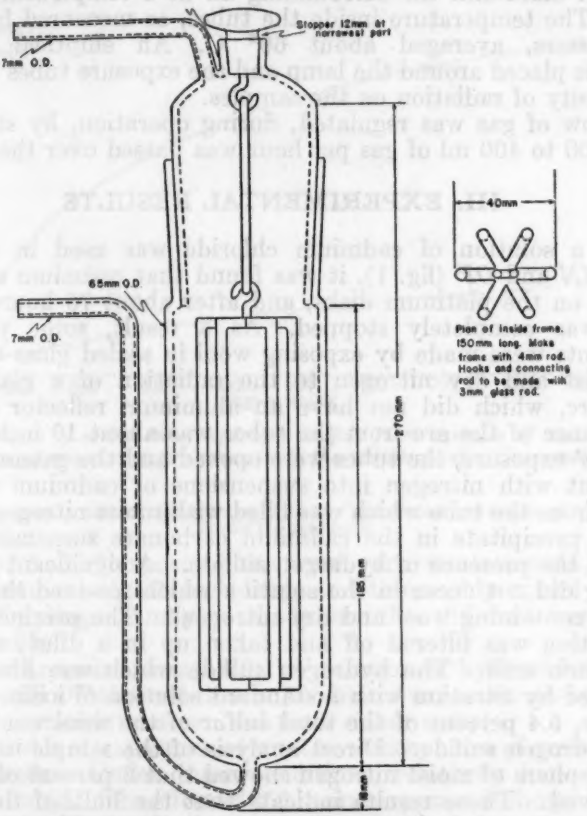
Stopper 12mm at narrowest part
7mm O.D.
65mm O.D.
7mm O.D.
40mm
Plan of inside frame. 150mm long. Make frame with 4mm rod. Hooks and connecting rod to be made with 3mm glass rod.
270 mm
105 mm
30 mm

FIGURE 2.—*Detailed drawing of the hexagonal glass framework on which the wool is mounted, and of the tube in which the wool is exposed.*

separate experiment the towers *MN* and *OP* were filled with the same solution. The solutions were as follows: 0.1 *N* solution of hydrochloric acid for the absorption of ammonia; a solution containing 10 g of sodium hydroxide and 10 g of bromine per liter for the absorption of hydrogen sulfide; and a 15-percent solution of cadmium chloride for determining whether the evolved gas was hydrogen sulfide or sulfur dioxide.

Figure 2 is a detailed drawing of the exposure tubes *K* and *L*.

[4] It was shown that when 210 liters of air, saturated with moisture, was dried by passing over anhydrous magnesium perchlorate at 25° C at the rate of from 1.5 to 3.5 liters per hour, the residual air did not contain a weighable amount of water [9].

Single-ply wool yarn [6] of very low twist was wound on the hexagonal glass framework. The ground-glass stopper, from which the frame is suspended, permits the frame to be revolved at frequent intervals, which assures fairly uniform exposures. Difficulties encountered in using ordinary lubricants in the large ground-glass joint, were overcome by using a glycol-phthalic anhydride resin [3].

The exposure tubes are 10 inches from the carbon arc. A fan, regulated by a bimetallic thermostat, is mounted below the exposure tubes and maintains the surrounding air at a temperature of about 35° C. The temperature inside the tubes, as measured by mercury thermometers, averaged about 60° C. An elliptical aluminum reflector is placed around the lamp and the exposure tubes to increase the intensity of radiation on the samples.

The flow of gas was regulated, during operation, by stopcocks *F* and *G*; 300 to 400 ml of gas per hour was passed over the wool.

III. EXPERIMENTAL RESULTS

When a solution of cadmium chloride was used in absorption towers *MN* and *OP* (fig. 1), it was found that cadmium sulfide precipitated on the platinum disks, and after about 75 hours, the flow of gas was completely stopped. As a result, some preliminary experiments were made by exposing wool in sealed glass tubes filled with moist and dry nitrogen to the radiation of a glass-enclosed carbon arc, which did not have an aluminum reflector around it. The distance of the arc from the tubes was about 10 inches. After 575 hours' exposure, the tubes were opened and the gaseous contents driven out with nitrogen into suspensions of cadmium carbonate. The gas from the tube which was filled with moist nitrogen produced a yellow precipitate in the cadmium carbonate suspensions, which indicated the presence of hydrogen sulfide. A significant amount of yellowing did not occur in the solution which received the gas from the tube containing wool and dry nitrogen.[6] The precipitate in the first solution was filtered off and taken up in a dilute solution of hydrochloric acid. The hydrogen sulfide which was liberated was determined by titration with a standard solution of iodine. By this procedure, 5.4 percent of the total sulfur of the wool was accounted for as hydrogen sulfide. Direct analysis of the sample irradiated in the atmosphere of moist nitrogen showed that 6 percent of the sulfur was evolved. These results indicate that the bulk of the sulfur is evolved from wool during irradiation in the form of hydrogen sulfide and not as sulfur dioxide,[7] as suggested by King [4] and by Meunier and Rey [5].

The rate at which hydrogen sulfide was evolved during irradiation in nitrogen was determined. The wool was wound on the hexagonal glass frames and dried at 105° C for 6 hours, after which it was rapidly transferred to the tubes *K* and *L*. The latter were covered with black paper, the light was turned on, and dry nitrogen passed over one sample and moist nitrogen over the other for 18 hours. The

[6] The yarn was prepared from raw wool which had been extracted with Stoddard solvent and washed with water. It was further purified by extraction in a Soxhlet apparatus with alcohol and ether, for 6 hours with each, and finally washed with water at 50° C.

[6] A comparison of the amount of sulfur lost from the sample irradiated in an atmosphere of moist nitrogen under these conditions with that lost by a sample under similar conditions irradiated in the new apparatus described in this paper indicates that the intensity of the radiation is greatly increased by the aluminum reflector.

[7] If any sulfur dioxide were present, it would react with hydrogen sulfide as follows:

$$SO_2 + 2H_2S \longrightarrow 2H_2O + 3S$$

paper was then removed and the exposures were started. The absorption pipettes *MN* and *OP* contained the alkaline bromine solution and any sulfide sulfur evolved was immediately oxidized to sulfate. At various intervals these solutions were removed and the amount of sulfate was determined as barium sulfate. The rates at which sulfur, in the form of hydrogen sulfide, is evolved from the wool are shown in figure 3.

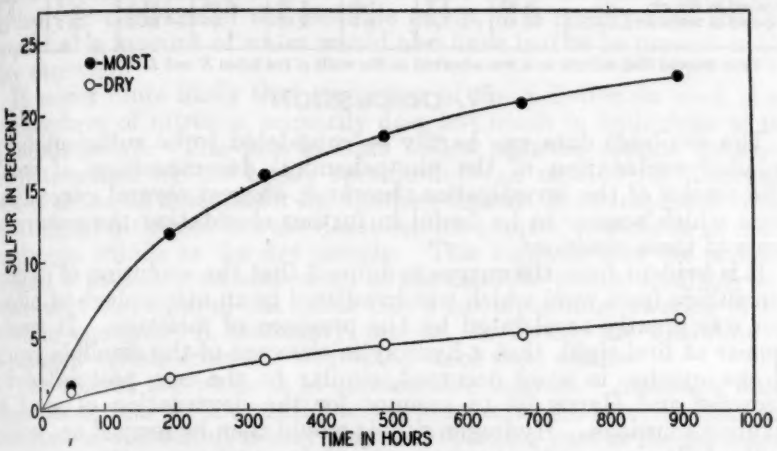

FIGURE 3.—*Rate of evolution of hydrogen sulfide from samples of wool exposed in atmospheres of moist and dry nitrogen to the radiation of a glass-enclosed carbon arc.*

The ordinate values are in terms of the percentage of the total sulfur which was evolved as hydrogen sulfide during the irradiation.

After 900 hours' exposure, the wool yarn was removed, cut into lengths about one-eighth inch long, and thoroughly mixed to assure uniform sampling. Analyses made on the different samples are shown in table 1.

A similar exposure, using a 0.1 *N* solution of hydrochloric acid in tubes *MN* and *OP* showed that in 305 hours' exposure, no appreciable amount of ammonia was evolved from either sample.

A third series of exposures of wool in atmospheres of moist and dry air were made. Under these conditions, relatively little hydrogen sulfide was found. The effect of 266 hours' exposure is shown in table 2.

TABLE 1.—*Effect on wool of 900 hours' exposure in atmospheres of moist and dry nitrogen to the radiation from a glass-enclosed carbon arc*

Sample	Total nitrogen	Ammonia nitrogen	Cystine	Total sulfur	Sulfur found in gases	Total sulfur accounted for	Alkali solubility	Sulfur as sulfuric acid
	%	mg/g	%	%	%	%	%	%
Unexposed	16.22	0.5	10.7	3.41	----------	100.0	15.9	None.
Exposed in dry nitrogen	16.17	.7	4.2	3.17	0.22	97.2	31.8	Do.
Exposed in moist nitrogen	16.26	.6	2.9	2.42	.79	[1] 92.0	36.9	Do.

[1] It was subsequently shown that some hydrogen sulfide was adsorbed on the walls of tube *K* through which moist nitrogen was passed.

TABLE 2.—*Effect on wool of 266 hours' exposure in atmospheres of moist and dry air to the radiation of a glass-enclosed carbon arc*

Sample	Total nitrogen	Ammonia nitrogen	Cystine	Total sulfur	Sulfur in gases	Total sulfur accounted for	Alkali solubility	Sulfur as sulfuric acid (on wool)
	%	mg/g	%	%	%	%	%	%
Original sample	16.22	0.5	10.7	3.49	----------	100.0	15.9	----------
Exposed in dry air	15.87	1.7	5.3	3.16	0.06	[1] 94.5	74.5	0.41
Exposed in moist air	15.81	1.4	5.5	3.00	.05	[1] 89.5	75.7	.39

[1] Tests showed that sulfuric acid was adsorbed on the walls of the tubes *K* and *L*.

IV. DISCUSSION

The available data can hardly be considered to be sufficient for a detailed explanation of the photochemical decomposition of wool. The results of the investigation, however, suggest several generalizations which appear to be useful in further elucidating the nature of some of these reactions.

It is evident from the curves in figure 3 that the evolution of hydrogen sulfide from wool which was irradiated in an atmosphere of nitrogen was greatly accelerated by the presence of moisture. It would appear at first sight, that a hydrolytic cleavage of the disulfide group of the cystine in wool occurred, similar to the one postulated by Crowder and Harris [6] to account for the degradation of wool in alkaline solutions. Hydrogen sulfide would then be formed according to the following reactions:

$$-CH_2-S-S-CH_2-+H_2O \rightleftharpoons -CH_2SH+-CH_2SOH \quad (1)$$
$$\downarrow$$
$$-CHO+H_2S$$

Assuming the above mechanism, it could be argued that in view of the great difficulty in obtaining absolutely dry wool, it is questionable whether all of the moisture was removed from the so-called dry sample at the start of these experiments. In other words, it would be difficult to tell whether the hydrogen sulfide obtained from the sample exposed in the atmosphere of dry nitrogen resulted from the decomposition of absolutely dry wool, or whether it was influenced by moisture which may still have been present.

If the photochemical decomposition of wool primarily involves a hydrolytic cleavage of the disulfide group, it must be pointed out, that of any moisture remaining on the fibers, some might be used up in photochemical reactions in the early stages of the exposure, but the rest would be rapidly removed by the warm, dry nitrogen which was continually passing over the sample. Under such conditions, there would be anticipated an initial, relatively rapid evolution of hydrogen sulfide, but the rate would soon decrease until practically no further evolution of gas occurred. That this is not so is indicated by the lower curve in figure 3.

If the decomposition proceeded according to equation 1, it would also be expected that the decrease in cystine content would increase with increasing alkalinity of the sample since the sulfenic acid group (—SOH) becomes increasingly unstable with increasing pH. That the reverse of this actually occurs was demonstrated by the authors in their earlier investigations [1] in which it was shown that the cystine content of a sample of wool treated with 0.1 *N* hydrochloric

acid and irradiated 100 hours decreased 52 percent, whereas that of a sample treated with a 0.1 *N* solution of sodium carbonate and exposed for the same time decreased only 35 percent.

Finally, it is evident from the data in table 1 that although the moist sample lost more than four times as much sulfur as the dry sample, the cystine content of the former is only slightly lower than that of the latter. A large portion of the cystine is destroyed during the irradiation, and if it is assumed that the destruction involves a hydrolytic cleavage of the disulfide group, it is readily seen that an appreciable amount of water would also have had to be present in the dry sample.

It seems more likely that the action of the radiation on wool in an atmosphere of nitrogen primarily does not result in hydrolysis of the disulfide group. The data in table 1 show that the cystine contents, as determined by the highly specific Sullivan method [7], decreased about the same amount for the samples exposed in atmospheres of dry or of moist nitrogen, but the moist sample evolved four times as much hydrogen sulfide as the dry sample. This suggests that the primary action is probably an activation of the disulfide group, resulting in a change in the state of the sulfur and a corresponding lowering of the cystine content. A secondary process, involving the evolution of hydrogen sulfide from the irradiated wool then occurs.

The role of the water is of considerable interest. Although water does not appear to be essential to the process, which involves changing the state of the sulfur, it may play an important part in the secondary reaction. That it might conceivably catalyze the secondary reaction, or actually react with products of the primary reaction to liberate hydrogen sulfide, was demonstrated by immersing samples of irradiated wool in warm water. Considerable hydrogen sulfide was evolved, but under similar conditions, a significant amount of hydrogen sulfide was not obtained from untreated wool.

The photochemical reactions which occur when wool is irradiated in atmospheres of moist and dry air are even more complex. In addition to the attack on the sulfur, nitrogen groups are affected, as shown in table 2. The increase in ammonia nitrogen content results from photo-oxidation processes [8]. Only a relatively small amount of hydrogen sulfide is evolved, the bulk of it being immediately oxidized to sulfuric acid. The acid thus formed further catalyzes the photochemical decomposition [1], which accounts for the high alkali-solubilities. The moist sample lost more sulfur, but again the cystine contents and the alkali-solubilities of both the moist and dry sample were changed about the same amount.

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